Microwave and Infrared Spectra of Free Radicals and Molecular Ions

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Contents

Eizi Hirota was born in 1930 in Osaka, Japan. He graduated from Department of Chemistry, Faculty of Science, the University of Tokyo in 1953 and continued the graduate study at the same place under the direction of Professor Yonezo Morino. He was appointed as a research associate at Department of Chemistry of the University of Tokyo in 1958 and received Ph.D. in 1959. He joined Professor E. Bright Wilson's group at Harvard University as a research fellow in 1960 and stayed there for two years. After returning to the University of Tokyo, he was promoted to Lecturer in 1962 and to Associate Professor in 1964. He became a Professor of the Department of Chemistry, Faculty of Science, at Kyushu University in 1968. When the Institute for Molecular Science was founded in Okazaki in 1975, he joined the Institute as the Chairman of the Department of Molecular Structure. In 1990 he was appointed to Vice-President of the Graduate University for Advanced Studies. He is also Professor-Emeritus of the Institute for Molecular Science. He has been working in the field of high-resolution molecular spectroscopy and its applications to large-amplitude motions in molecules and to the detection and structure determination of transient species.

I. Introduction

Chemists devised the idea of intermediate species in order to explain the mechanisms of chemical reactions. Therefore, these intermediate molecules first appeared in a sort of hypothetical existence. However, as physical methods were developed, many reaction intermediates were, in fact, confirmed to exist through the observation of signals to which these species gave rise. One of the most important developments along this line was the invention of flash photolysis in 1949.[1] This method allows one to generate transient species at concentrations large enough to observe their spectra. It also gives information on the lifetime of these species. Another important direction was brought about by matrix isolation in the 1950s.[2] Transient species were either produced in the gaseous phase by some appropriate methods like electrical discharge in a precursor diluted with a large amount of inert gas and were then deposited on a cold surface with the buffer gas, or generated directly in an inert gas matrix by photolysis or photolysis-induced chemical reactions of precursors.

Spectroscopic techniques also made remarkable progress after World War II. Electronic spectroscopy using a large grating spectrograph was combined with flash photolysis in an ingeneous way.[3] Faint signals of transient species were recorded on photographic plates of high sensitivity. The use of plates was particularly

suited for detection and observation of these species generated by flash photolysis.

To species trapped in a low-temperature matrix, we may apply various types of conventional spectroscopic methods. Among them electron spin resonance (ESR) or electron paramagnetic resonance (EPR) spectroscopy has proved to be most useful, because it pinpoints the paramagnetism of transient species. The structures of these molecules were elucidated through the observed hyperfine structure. Electronic and vibrational spectroscopy has also yielded much information on trapped transient species. However, all these data obtained on low-temperature matrices are subject to matrix effects, and it is obviously indispensable to compare the matrix data with those in the gaseous phase, in order to assess the matrix effects. The gas-phase data act as a sort of reference, but they were, and still are, rather sparse.

It was almost impossible up to around 1960 to apply infrared and microwave spectroscopy to transient molecules in the gaseous phase. Many attempts were made, but few successful cases were reported.[4,5] How-

ever, a new epoch was made around the late 1960s for spectroscopy in these long-wavelength regions. Microwave spectroscopy was extended to millimeter- and submillimeter-wave regions; although these regions had been accessible to a limited number of laboratories, they became open to others as well, thanks to development of multipliers of high efficiency, which became available commercially. Because the absorption coefficient of the rotational transition is proportional to the square or the cube of its frequency, this extension of the working region to short wavelengths results in a dramatic increase of the effective sensitivity of the method.

Lasers came into use also around this time. The water and the hydrogen cyanide lasers in the far-infrared region and the carbon dioxide, the nitrous oxide, and the carbon monoxide lasers in the infrared region act as best examples among others. Because these lasers are fixed in frequency, they were combined with electric-field or magnetic-field tuning of molecular transitions. In particular, the latter, referred to as laser magnetic resonance or LMR, has played an important role in the study of free radicals.[6]

The high brightness of lasers has improved the sensitivity of infrared spectroscopy by orders of magnitude. In addition, the development of tunable sources has greatly expanded the versatility of infrared laser spectroscopy; the diode laser in nearly the entire infrared region, the color or F center laser in 2–3.5 μm, and the difference frequency generation in 2–5 μm by mixing the outputs of a dye laser and an argon ion laser in a nonlinear element have been employed most widely.

The present article focuses attention primarily on high-resolution spectroscopy in the wavelength regions from near-infrared to radio frequency which has been devoted to the study of transient species. Although the experimental details will not be included in this article, a few features characteristic of these spectroscopic methods may be relevant for the discussion of the results. The electronic state of primary concern is obviously the ground state, although there are a few exceptions where electronic transitions appear in the infrared. This might be thought of as a serious limitation of spectroscopy in the longer wavelength region. However, because the ground electronic state is free of predissociation in almost all cases, the high-resolution inherent in the method is completely guaranteed. Infrared spectroscopy records spectral lines with a width mainly determined by the Doppler effect, provided that the sample pressure does not exceed about 10 Torr, and allows us to observe Doppler-free spectral lines by exploiting nonlinear effects. The resolution is even higher in microwave spectroscopy. Therefore, fine and hyperfine structure and the discussion of molecular structure based on these fine details are the primary concern of spectroscopic studies in longer wavelength regions.

Although the present article is limited to the results obtained by infrared and microwave spectroscopy, other spectroscopic results and theoretical studies such as those based on ab initio calculations will be cited wherever appropriate for the discussion.

The transient molecules to be included in the present article comprise wide varieties. Free radicals, which are defined in the present article to be species that contain (an) unpaired electron(s), constitute certainly the main group, but the species that are stable and can be easily

isolated will be excluded from the discussion, e.g. O_2, NO, and NO_2. On the other hand, some "singlet" molecules are included. It is because they play important roles as reaction intermediates in various processes. An example is silylene SiH_2. Ionic species are naturally considered, irrespective of whether unpaired electrons are present or not.

Transient species are grouped according to their structures, and each group is given a table which lists all references concerning the transient molecules in this group investigated by high-resolution spectroscopy in the long-wavelength regions. Thus the present article consists primarily of tables of references with some appropriate comments as to which method was employed and what sort of information was obtained. The tables thus prepared are listed as follows Table I. Atomic Species, Table II. Diatomic Hydrides, Table III. Diatomic Radicals, Table IV. Linear Radicals, Table V. Symmetric-Top Free Radicals, Table VI. Asymmetric-Top Free Radicals, and Table VII. Ionic Species. The main emphasis is placed on spectroscopy, and references devoted primarily to related areas such as chemical reaction and astronomy are thus far from complete. For each group some topical problems are discussed in some detail. The discussion will serve to clarify characteristic features of the species in each group.

There are a number of books and review articles pertinent to transient species. Huber and Herzberg[7] summarized all references of studies on diatomic molecules up to around 1977. Jacox has published three review articles on polyatomic transient molecules and ions.[8-10] The first one appearing in 1984 lists all references on about 480 covalently bonded transient molecules consisting of up to 16 atoms. It is supplemented by the second one published in 1988, which is limited to up to 6-atomic species, but covers approximately 500 neutral and ionic molecules. The third one appears around the end of 1990 as a supplement to the two previous ones; it includes about 500 neutral and ionic transient molecules consisting of up to 16 atoms. Jacox now stores all bibliographical data in floppy disks and makes them available to the public upon request. Hirota[11a] published a book on transient molecules studied by high-resolution spectroscopy. After the present article was completed, a review paper by Bernath[11b] on infrared spectroscopy of transient molecules appeared.

Molecular ions have recently attracted much attention, and have evoked a number of spectroscopic studies in the wavelength region of present concern. The results have been reviewed in a number of publications. Two books are mentioned here: one edited by Miller and Bondybey[12] and the other by Maier.[13] A few review articles have also appeared.[14] A discussion meeting was arranged by the Royal Society London.[15]

II. Implications of Fine and Hyperfine Structure Constants

The unpaired electron characterizes the free radical. It is accompanied by spin and orbital angular momenta, which cause splittings in the spectrum of the free radical.

TABLE I. Atomic Species[a]

species	ref (method and comment)	species	ref (method and comment)
He	Miller, T. A.; Freund, R. S. *Phys. Rev.* 1971, *A4*, 81 (EPR)	O	Davies, P. B.; Handy, B. J.; Murray Lloyd, E. K.; Smith, D. R. *J. Chem. Phys.* 1978, *68*, 1135 (FIR LMR)
	Miller, T. A.; Freund, R. S. *Phys. Rev.* 1972, *A5*, 588 (EPR)		Saykally, R. J.; Evenson, K. M. *J. Chem. Phys.* 1979, *71*, 1564 (FIR LMR)
	Rosenbluth, M.; Panock, R.; Lax, B.; Miller, T. A. *Phys. Rev.* 1978, *A18*, 1103 (IR LMR)		Brown, P. R.; Davies, P. B.; Johnson, S. A. *Chem. Phys. Lett.* 1987, *133*, 239 (IR diode, Rydberg levels)
	Panock, R.; Rosenbluth, M.; Lax, B.; Miller, T. A. *Phys. Rev.* 1980, *A22*, 1050 (IR LMR)		Zink, L. R.; Evenson, K. M.; Matsushima, F.; Nelis, T.; Robinson, R. L. *Astrophys. J.* 1991, *371*, L85 (tunable FIR)
	Le, H.; Rosenbluth, M.; Lax, B.; Miller, T. A. *Phys. Rev.* 1981, *A24*, 3111 (LMR)	F	Stanton, A. C.; Kolb, C. E. *J. Chem. Phys.* 1980, *72*, 6637 (IR diode)
	Rosenbluth, M.; Le, H.; Lax, B.; Panock, R.; Miller, T. A. *Opt. Lett.* 1981, *6*, 99 (FIR LMR)	Cl	Dagenais, M.; Johns, J. W. C.; McKellar, A. R. W. *Can. J. Phys.* 1976, *54*, 1438 (IR LMR)
	Nagai, K.; Tanaka, K.; Hirota, E. *J. Phys. B: At. Mol. Phys.* 1982, *15*, 341 (IR diode)		Davies, P. B.; Russell, D. K. *Chem. Phys. Lett.* 1979, *67*, 440 (IR diode)
	Sears, T. J.; Foster, S. C.; McKellar, A. R. W. *J. Opt. Soc. Am.* 1986, *B3*, 1037 (IR diode)		Braun, V. R.; Krasnoperov, L. N.; Panfilov, V. N. *Opt. Spectrosc.* 1982, *52*, 428 (IR LMR)
Ne, Ar	Begemann, M. H.; Saykally, R. J. *Opt. Commun.* 1982, *40*, 277 (color)		Chichinin, A. I.; Krasnoperov, L. N. *Chem. Phys. Lett.* 1986, *124*, 8 (IR LMR, relaxation)
	Yamada, C.; Kanamori, H.; Hirota, E. *J. Chem. Phys.* 1985, *83*, 552 (IR diode)		Chasovnikov, S. A.; Chichinin, A. I.; Krasnoperov, L. N. *Chem. Phys.* 1987, *116*, 91 (IR LMR, reaction)
Kr, Xe	Sears, T. J.; McKellar, A. R. W. *Can. J. Phys.* 1982, *60*, 345 (IR LMR)		Tiemann, E.; Kanamori, H.; Hirota, E. *J. Chem. Phys.* 1988, *88*, 2457 (IR diode)
Li, Ba	Begemann, M. H.; Saykally, R. J. *Opt. Commun.* 1982, *40*, 277 (color)		Chichinin, A. I.; Krasnoperov, L. N. *Chem. Phys. Lett.* 1989, *160*, 448 (IR LMR)
C	Saykally, R. J.; Evenson, K. M. *Astrophys. J.* 1980, *238*, L107 (FIR LMR)	Br	Kasper, J. V. V.; Pollock, C. R.; Curl, R. F., Jr.; Tittel, F. K. *Chem. Phys. Lett.* 1981, *77*, 211 (color)
	Jaffe, D. T.; Harris, A. I.; Silber, M.; Genzel, R.; Betz, A. L. *Astrophys. J.* 1985, *290*, L59 (FIR astronomy)		Adams, H.; Hall, J. L.; Russell, L. A.; Kasper, J. V. V.; Tittel, F. K.; Curl, R. F., Jr. *J. Opt. Soc. Am.* 1985, *B2*, 776 (color)
	Cooksy, A. L.; Blake, G. A.; Saykally, R. J. *Astrophys. J.* 1986, *305*, L89 (FIR LMR)		Haugen, H. K.; Weitz, E.; Leone, S. R. *Chem. Phys. Lett.* 1985, *119*, 75 (color)
	Zmuidzinas, J.; Betz, A. L.; Goldhaber, D. M. *Astrophys. J.* 1986, *307*, L75 (radioastronomy)	Mg	Inguscio, M.; Leopold, K. R.; Murray, J. S.; Evenson, K. M. *J. Opt. Soc. Am.* 1985, *B2*, 1566 (FIR LMR)
	Cooksy, A. L.; Saykally, R. J.; Brown, J. M.; Evenson, K. M. *Astrophys. J.* 1986, *309*, 828 (FIR LMR)		Lemoine, B.; Demuynck, C.; Destombes, J. L. *Astron. Astrophys.* 1988, *191*, L4 (IR diode, Rydberg levels, Zeeman effect)
	Davies, P. B.; Martin, P. A. *Astron. Astrophys.* 1988, *199*, L13 (IR diode).		Lemoine, B.; Petitprez, D.; Destombes, J. L.; Chang, E. S. *J. Phys. B At. Mol. Opt. Phys.* 1990, *23*, 2217S (IR diode)
	Yamamoto, S.; Saito, S. *Astrophys. J.* 1991, *370*, L103 (submm wave)	Hg	Johns, J. W. C.; McKellar, A. R. W.; Riggin, M. *J. Chem. Phys.* 1977, *66*, 3962 (IR LMR)
N	Crampton, S. B.; Berg, H. C.; Robinson, H. G.; Ramsey, N. F. *Phys. Rev. Lett.* 1970, *24*, 195 (rf spectroscopy)		
	Diebold, G. J.; McFadden, D. L. *Phys. Rev.* 1982, *A25*, 1504 (EPR)		
	Davies, P. B.; Martin, P. A. *Astron. Astrophys.* 1988, *199*, L13 (IR diode)		
	Bogey, M.; Davies, P. B.; Davis, I. H.; Destombes, J. L. *Astrophys. J.* 1989, *339*, L49 (mm wave)		
	Bley, U.; Koch, M.; Temps, F.; Davies, P. B.; Davis, I. H. *J. Chem. Phys.* 1989, *90*, 628 (FIR LMR)		

[a] Abbreviations for the method employed are as follows: EPR, electron paramagnetic resonance; IR LMR, infrared laser magnetic resonance; IR diode, infrared diode laser; color, color center or F center laser; FIR LMR, far-infrared laser magnetic resonance; radioastronomy, observation by a radiotelescope; submm wave, submillimeter wave; rf spectroscopy, radio frequency spectroscopy; mm wave, millimeter wave; tunable FIR, tunable far-infrared source.

A. Fine Structure

In cases where only the unpaired electron spin is, but no nuclear spins are, responsible for these splittings, they are referred to as fine structure. The spin–orbit interaction, namely the interaction between the unpaired electron spin and orbital angular momenta is the most important term among the fine structure interactions. However, it has diagonal matrix elements only for electronic states where the unpaired electron orbital angular momentum is not quenched. This normally holds for linear molecules, in which the unpaired electron is subjected to a cylindrically symmetric field, preserving the axial component of the orbital angular momentum. Otherwise, the orbital angular momentum is largely quenched, even in a symmetric-top molecule.

In nonlinear molecules the spin–orbit interaction may be combined with the orbital–rotation interaction to result in the spin–rotation interaction, the most rep-

resentative fine structure interaction in this type of molecule. For a nonlinear molecule the interaction is represented by a tensor ϵ, and its diagonal term, ϵ_{bb} for example, is given by

$$\epsilon_{bb} = 4\mathrm{Re}\sum(-1)^{sn}\langle 0|A_{SO}L_b|n\rangle\langle n|BL_b|0\rangle/[E(n) - E(0)] \quad (1)$$

where Re denotes the real part, 0 and n denote, respectively, the ground state and an excited electronic state, and the parity factor $(-1)^{sn}$ is equal to either $+1$ or -1, depending on the type of excitation $0 \rightarrow n$.

In a linear molecule, the component of the total angular momentum along the molecular axis is preserved, and thus, when it is finite, the state is doubly degenerate, because the state energy is independent of the plus and minus signs of the component. This degeneracy may be lifted again by the interaction of the orbital angular momentum with the rotational motion.

TABLE II. Diatomic Hydrides[a]

species[b]	ref (method and comment)	species[b]	ref (method and comment)
LiH	James, T. C.; Norris, W. G.; Klemperer, W. J. Chem. Phys. 1960, 32, 728 (IR)		Nelis, Th.; Bachem, E.; Bohle, W.; Urban, W. Mol. Phys. 1988, 64, 759 (IR LMR)
	Lawrence, T. R.; Anderson, C. H.; Ramsey, N. F. Phys. Rev. 1963, 130, 1865 (mol beam, g_r)		Lipus, K.; Simon, U.; Bachem, E.; Nelis, Th.; Urban, W. Mol. Phys. 1989, 67, 1431 (IR LMR)
(LiD)	Pearson, E. F.; Gordy, W. Phys. Rev. 1969, 177, 59 (mm wave)		Steimle, T. C.; Nachman, D. F.; Shirley, J. E.; Fletcher, D. A.; Brown, J. M. Mol. Phys. 1990, 69, 923 (MODR, Λ-doubling, hfs)
	Rothstein, E. J. Chem. Phys. 1969, 50, 1899; 1970, 52, 2804 (mol beam)		Nelis, Th.; Beaton, S. P.; Evenson, K. M.; Brown, J. M. J. Mol. Spectrosc. 1991, 148, 462 (FIR LMR, hfs)
(LiD)	Freeman, R. R.; Jacobson, A. R.; Johnson, D. W.; Ramsey, N. F. J. Chem. Phys. 1975, 63, 2597 (mol beam, hfs)		Bachem, E.; Urban, W.; Nelis, Th. Mol. Phys. 1991, 73, 1031 (IR LMR)
(LiD)	Plummer, G. M.; Herbst, E.; De Lucia, F. C. J. Chem. Phys. 1984, 81, 4893 (submm wave)	CuH	Ram, R. S.; Bernath, P. F.; Brault, J. W. J. Mol. Spectrosc. 1985, 113, 269 (FTIR)
	Plummer, G. M.; Herbst, E.; De Lucia, F. C. Astrophys. J. 1984, 282, L113 (submm wave)		Beaton, S. P.; Evenson, K. M. J. Mol. Spectrosc. 1990, 142, 336 (tunable FIR)
	Yamada, C.; Hirota, E. J. Chem. Phys. 1988, 88, 6702 (IR diode)	AgH	Birk, H.; Jones, H. Chem. Phys. Lett. 1989, 161, 27 (IR diode)
(LiD)	Maki, A. G.; Olson, Wm. B.; Thompson, G. J. Mol. Spectrosc. 1990, 144, 257 (FTIR)	(AgD)	Urban, R.-D.; Birk, H.; Polomsky, P.; Jones, H. J. Chem. Phys. 1991, 94, 2523 (IR diode)
NaH (NaD)	Sastry, K. V. L. N.; Herbst, E.; De Lucia, F. C. J. Chem. Phys. 1981, 75, 4753 (mm wave)	ZnH	Urban, R.-D.; Magg, U.; Birk, H.; Jones, H. J. Chem. Phys. 1990, 92, 14 (IR diode)
(NaD)	Sastry, K. V. L. N.; Herbst, E.; De Lucia, F. C. Astrophys. J. 1981, 248, L53 (mm and submm wave)	(ZnD)	Birk, H.; Urban, R.-D.; Polomsky, P.; Jones, H. J. Chem. Phys. 1991, 94, 5435 (IR diode)
	Leopold, K. R.; Zink, L. R.; Evenson, K. M.; Jennings, D. A. J. Mol. Spectrosc. 1987, 122, 150 (FIR)	CdH	Urban, R.-D.; Magg, U.; Birk, H.; Jones, H. J. Chem. Phys. 1990, 92, 14 (IR diode)
	Magg, U.; Jones, H. Chem. Phys. Lett. 1988, 146, 415 (IR diode)	(CdD)	Birk, H.; Urban, R.-D.; Polomsky, P.; Jones, H. J. Chem. Phys. 1991, 94, 5435 (IR diode)
	Maki, A. G.; Olson, W. B. J. Chem. Phys. 1989, 90, 6887 (FTIR)	BH	Pianalto, F. S.; O'Brien, L. C.; Keller, P. C.; Bernath, P. F. J. Mol. Spectrosc. 1988, 129, 348 (FT emission)
KH	Haese, N. N.; Liu, D.-J.; Altman, R. S. J. Chem. Phys. 1984, 81, 3766 (IR diode)	AlH($X^1\Sigma^+$)	Deutsch, J. L.; Neil, W. S.; Ramsay, D. A. J. Mol. Spectrosc. 1987, 125, 115 (FTIR, emission)
RbH	Magg, U.; Birk, H.; Jones, H. Chem. Phys. Lett. 1988, 151, 503 (IR diode)	GaH	Urban, R.-D.; Magg, U.; Jones, H. Chem. Phys. Lett. 1989, 154, 135 (IR diode)
CsH	Magg, U.; Jones, H. Chem. Phys. Lett. 1988, 148, 6 (IR diode)	(GaD)	Urban, R.-D.; Birk, H.; Polomsky, P.; Jones, H. J. Chem. Phys. 1991, 94, 2523 (IR diode)
MgH	Leopold, K. R.; Zink, L. R.; Evenson, K. M.; Jennings, D. A.; Mizushima, M. J. Chem. Phys. 1986, 84, 1935 (FIR)	InH	Bahnmaier, A. H.; Urban, R.-D.; Jones, H. Chem. Phys. Lett. 1989, 155, 269 (IR diode)
(MgD)	Lemoine, B.; Demuynck, C.; Destombes, J. L.; Davies, P. B. J. Chem. Phys. 1988, 89, 673 (IR diode)	(InD)	Urban, R.-D.; Birk, H.; Polomsky, P.; Jones, H. J. Chem. Phys. 1991, 94, 2523 (IR diode)
	Zink, L. R.; Jennings, D. A.; Evenson, K. M.; Leopold, K. R. Astrophys. J. 1990, 359, L65 (tunable FIR)	TlH	Urban, R.-D.; Bahnmaier, A. H.; Magg, U.; Jones, H. Chem. Phys. Lett. 1989, 158, 443 (IR diode)
CaH (CaD)	Petitprez, D.; Lemoine, B.; Demuynck, C.; Destombes, J. L.; Macke, B. J. Chem. Phys. 1989, 91, 4462 (IR diode)	(TlD)	Urban, R.-D.; Birk, H.; Polomsky, P.; Jones, H. J. Chem. Phys. 1991, 94, 2523 (IR diode)
SrH	Magg, U.; Birk, H.; Jones, H. Chem. Phys. Lett. 1988, 151, 263 (IR diode)	CH	Evenson, K. M.; Radford, H. E.; Moran, Jr., M. M. Appl. Phys. Lett. 1971, 18, 426 (FIR LMR)
(SrD)	Birk, H.; Urban, R.-D.; Polomsky, P.; Jones, H. J. Chem. Phys. 1991, 94, 5435 (IR diode)		Rydbeck, O. E. H.; Elldér, J.; Irvine, W. M. Nature 1973, 246, 466 (radioastronomy)
BaH	Magg, U.; Birk, H.; Jones, H. Chem. Phys. Lett. 1988, 149, 321 (IR diode)		Turner, B. E.; Zuckerman, B. Astrophys. J. 1974, 187, L59 (radioastronomy)
(BaD)	Birk, H.; Urban, R.-D.; Polomsky, P.; Jones, H. J. Chem. Phys. 1991, 94, 5435 (IR diode)		Hougen, J. T.; Mucha, J. A.; Jennings, D. A.; Evenson, K. M. J. Mol. Spectrosc. 1978, 72, 463 (FIR LMR)
CrH($X^6\Sigma^+$)	Corkery, S. M.; Brown, J. M.; Beaton, S. P.; Evenson, K. M. J. Mol. Spectrosc. 1991, 149, 257 (FIR LMR, fs and hfs)		Brazier, C. R.; Brown, J. M. J. Chem. Phys. 1983, 78, 1608 (MODR)
	Lipus, K.; Bachem, E.; Urban, W. Mol. Phys. 1991, 73, 1041 (IR LMR)		Brown, J. M.; Evenson, K. M. J. Mol. Spectrosc. 1983, 98, 392 (FIR LMR)
MnH	Urban, R.-D.; Jones, H. Chem. Phys. Lett. 1989, 163, 34 (IR diode)		Bogey, M.; Demuynck, C.; Destombes, J. L. Chem. Phys. Lett. 1983, 100, 105 (MW, Λ-doublet)
(MnD)	Balfour, W.; Launila, O.; Klynning, L. Mol. Phys. 1990, 69, 443 (FTIR, electronic $c^5\Sigma$ - $a^5\Sigma$, $b^5\Pi_i$ - $a^5\Sigma$)		Lubic, K. G.; Amano, T. J. Chem. Phys. 1984, 81, 1655 (difference)
(MnD)	Urban, R.-D.; Jones, H. Chem. Phys. Lett. 1991, 178, 295 (IR diode)	(^{13}CH)	Brazier, C. R.; Brown, J. M. Can. J. Phys. 1984, 62, 1563 (MODR)
FeH	Beaton, S. P.; Evenson, K. M.; Nelis, T.; Brown, J. M. J. Chem. Phys. 1988, 89, 4446 (FIR LMR)		Steimle, T. C.; Woodward, D. R.; Brown, J. M. Astrophys. J. 1985, 294, L59 (MODR)
CoH	Beaton, S. P.; Evenson, K. M.; Nelis, T.; Brown, J. M. J. Chem. Phys. 1988, 89, 4446 (FIR LMR)	(^{13}CH)	Ziurys, L. M.; Turner, B. E. Astrophys. J. 1985, 292, L25 (radioastronomy)
	Lipus, K.; Nelis, Th.; Bachem, E.; Urban, W. Mol. Phys. 1989, 68, 1171 (IR LMR)		Steimle, T. C.; Woodward, D. R.; Brown, J. M. J. Chem. Phys. 1986, 85, 1276 (MODR)
NiH	Beaton, S. P.; Evenson, K. M.; Nelis, T.; Brown, J. M. J. Chem. Phys. 1988, 89, 4446 (FIR LMR)		Bernath, P. F. J. Chem. Phys. 1987, 86, 4838 (FT emission)
			Nelis, T.; Brown, J. M.; Evenson, K. M. J. Chem. Phys. 1988, 88, 2087 (FIR LMR, $a^4\Sigma$)
			Stacey, G. J.; Lugton, J. B.; Genzel, R. Astrophys. J. 1987, 313, 859 (radioastronomy)

TABLE II (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
	Mélen, F.; Grevesse, N.; Sauval, A. J.; Farmer, C. B.; Norton, R. H.; Bredohl, H.; Dubois, I. *J. Mol. Spectrosc.* **1989**, *134*, 305 (solar spectra)	(PD)	Ohashi, N.; Kawaguchi, K.; Hirota, E. *J. Mol. Spectrosc.* **1984**, *103*, 337 (FIR LMR)
(CD)	Brown, J. M.; Evenson, K. M. *J. Mol. Spectrosc.* **1989**, *136*, 68 (FIR LMR)		Anacona, J. R.; Davies, P. B.; Hamilton, P. A. *Chem. Phys. Lett.* **1984**, *104*, 269 (IR diode)
	Nelis, Th.; Brown, J. M.; Evenson, K. M. *J. Chem. Phys.* **1990**, *92*, 4067 (FIR LMR, $a^4\Sigma$)		Ram, R. S.; Bernath, P. F. *J. Mol. Spectrosc.* **1987**, *122*, 275 (FTIR)
	Bernath, P. F.; Brazier, C. R.; Olsen, T.; Hailey, R.; Fernando, W. T. M.; Woods, C.; Hardwick, J. L. *J. Mol. Spectrosc.* **1991**, *147*, 16; *149*, 563 (FTIR, electronic $A^2\Delta-X^2\Pi$, $B^2\Sigma-X^2\Pi$)	AsH	Kawaguchi, K.; Hirota, E. *J. Mol. Spectrosc.* **1984**, *106*, 423 (FIR LMR)
SiH	Knights, J. C.; Schmitt, J. P. M.; Perrin, J.; Guelachvili, G. *J. Chem. Phys.* **1982**, *76*, 3414 (FT absorption and emission)		Anacona, J. R.; Davies, P. B.; Johnson, S. A. *Mol. Phys.* **1985**, *56*, 989 (IR diode)
	Brown, J. M.; Robinson, D. *Mol. Phys.* **1984**, *51*, 883 (IR LMR)	BiH (BiD)	Bopegedera, A. M. R. P.; Brazier, C. R.; Bernath, P. F. *Chem. Phys. Lett.* **1989**, *162*, 301 (IR diode)
	Brown, J. M.; Curl, R. F.; Evenson, K. M. *J. Chem. Phys.* **1984**, *81*, 2884 (FIR LMR)		Fink, E. H.; Setzer, K. D.; Ramsay, D. A.; Vervloet, M.; Brown, J. M. *J. Mol. Spectrosc.* **1990**, *142*, 108 (FTIR, electronic A1–X0⁺)
	Davies, P. B.; Isaacs, N. A.; Johnson, S. A.; Russell, D. K. *J. Chem. Phys.* **1985**, *83*, 2060 (IR diode)		Urban, R.-D.; Polomsky, P.; Jones, H. *Chem. Phys. Lett.* **1991**, *181*, 485 (IR diode)
	Brown, J. M.; Curl, R. F.; Evenson, K. M. *Astrophys. J.* **1985**, *292*, 188 (FIR LMR)	OH	Sanders, T. M.; Schawlow, A. L.; Dousmanis, G. C.; Townes, C. H. *Phys. Rev.* **1953**, *89*, 1158 (MW)
	Betrencourt, M.; Boudjaadar, D.; Chollet, P.; Guelachvili, G.; Morillon-Chapey, M. *J. Chem. Phys.* **1986**, *84*, 4121 (FT emission)	(OD)	Dousmanis, G. C.; Sanders, T. M.; Townes, C. H. *Phys. Rev.* **1955**, *100*, 1735 (MW)
	Chollet, P.; Guelachvili, G.; Morillon-Chapey, M.; Gressier, P.; Schmitt, J. P. M. *J. Opt. Soc. Am.* **1986**, *B3*, 687 (FT emission)		Ehrenstein, G.; Townes, C. H.; Stevensen, M. J. *Phys. Rev. Lett.* **1959**, *3*, 40 (MW)
(isotopes)	Seebass, W.; Werner, J.; Urban, W.; Comben, E. R.; Brown, J. M. *Mol. Phys.* **1987**, *62*, 161 (IR LMR)		Radford, H. E. *Phys. Rev.* **1961**, *122*, 114 (EPR, Zeeman)
GeH	Brown, J. M.; Evenson, K. M.; Sears, T. J. *J. Chem. Phys.* **1985**, *83*, 3275 (FIR LMR)		Meyer, R. T.; Myers, R. J. *J. Chem. Phys.* **1961**, *34*, 1074 (MW, dipole moment)
	Towle, J. P.; Brown, J. M. *Mol. Phys.* **1990**, *70*, 161 (IR LMR)		Radford, H. E. *Phys. Rev.* **1962**, *126*, 1035 (EPR, Zeeman)
(GeD)	Zimmermann, W.; Smolka, K.-P.; Urban, W. *Mol. Phys.* **1990**, *70*, 167 (IR LMR)	(¹⁷OH)	Ehrenstein, G. *Phys. Rev.* **1963**, *130*, 669 (MW, hfs, and dipole moment)
	Akiyama, Y.; Tanaka, K.; Tanaka, T. *J. Chem. Phys.* **1991**, *94*, 3280 (IR diode)		Powell, F. X.; Lide, Jr., D. R. *J. Chem. Phys.* **1965**, *42*, 4201 (MW, dipole moment)
	Petri, M.; Simon, U.; Zimmermann, W.; Urban, W.; Towle, J. P.; Brown, J. M. *Mol. Phys.* **1991**, *72*, 315 (IR diode)		Johnson, D. R.; Lin, C. C. *J. Mol. Spectrosc.* **1967**, *23*, 201 (MW, Zeeman)
	Ashworth, S. H.; Brown, J. M. *Chem. Phys. Lett.* **1991**, *182*, 73 (IR LMR, μ from relative intensity)		Poynter, R. L.; Beaudet, R. A. *Phys. Rev. Lett.* **1968**, *21*, 305 (MW)
SnH(²Π)	Zimmermann, W.; Nelis, Th.; Bachem, E.; Pahnke, R.; Urban, W. *Mol. Phys.* **1989**, *68*, 199 (IR LMR)		Marshall, A.; de Zafra, R. L.; Metcalf, H. *Phys. Rev. Lett.* **1969**, *22*, 445 (level crossing)
(SnD)	Simon, U.; Petri, M.; Zimmermann, W.; Huhn, G.; Urban, W. *Mol. Phys.* **1991**, *73*, 1051 (IR diode)		Thacker, D. L.; Wilson, W. J.; Barrett, A. H. *Astrophys. J.* **1970**, *161*, L191 (radioastronomy)
PbH	Magg, U.; Jones, H. *Chem. Phys. Lett.* **1990**, *166*, 253 (IR diode)		Palmer, P.; Zuckerman, B. *Astrophys. J.* **1970**, *161*, L199 (radioastronomy)
NH	Lambert, D. L.; Beer, R. *Astrophys. J.* **1972**, *177*, 514 (IR astronomy)		Churg, A.; Levy, D. H. *Astrophys. J.* **1970**, *162*, L161 (EPR, excited vibrational states)
	Radford, H. E.; Litvak, M. M. *Chem. Phys. Lett.* **1975**, *34*, 561 (FIR LMR)	(¹⁷OH, OD)	Carrington, A.; Lucas, N. J. D. *Proc. R. Soc. Lond.* **1970**, *A314*, 567 (EPR, hfs)
(isotopes)	Wayne, F. D.; Radford, H. E. *Mol. Phys.* **1976**, *32*, 1407 (FIR LMR)		Murphy, R. E. *J. Chem. Phys.* **1971**, *54*, 4852 (IR emission)
	Van den Heuvel, F. C.; Meerts, W. L.; Dymanus, A. *Chem. Phys. Lett.* **1982**, *92*, 215 (tunable FIR)		d'Incan, J.; Effantin, C.; Roux, F. *J. Quant. Spectrosc. Rad. Transfer* **1971**, *11*, 1215 (FTIR, intensity)
	Bernath, P. F.; Amano, T. *J. Mol. Spectrosc.* **1982**, *95*, 359 (difference)		Clough, P. N.; Curran, A. H.; Thrush, B. A. *Proc. R. Soc. Lond.* **1971**, *A323*, 541 (EPR, excited vibrational states)
	Hall, J. L.; Adams, H.; Kasper, J. V. V.; Curl, R. F.; Tittel, F. K. *J. Opt. Soc. Am.* **1985**, *B2*, 781 (color, $a^1\Delta$)		Lee, K. P.; Tam, W. G.; Larouche, R.; Woonton, G. A. *Can. J. Phys.* **1971**, *49*, 2207 (EPR, excited vibrational states)
(ND)	Leopold, K. R.; Evenson, K. M.; Brown, J. M. *J. Chem. Phys.* **1986**, *85*, 324 (FIR LMR, $a^1\Delta$)		ter Meulen, J. J.; Dymanus, A. *Astrophys. J.* **1972**, *172*, L21 (beam maser)
	Boudjaadar, D.; Brion, J.; Chollet, P.; Guelachvili, G.; Vervloet, M. *J. Mol. Spectrosc.* **1986**, *119*, 352 (FT emission)		Kasuya, T.; Shimoda, K. *Jpn. J. Appl. Phys.* **1972**, *11*, 1571 (FIR LMR)
	Vasconcellos, E. C. C.; Davidson, S. A.; Brown, J. M.; Leopold, K. R.; Evenson, K. M. *J. Mol. Spectrosc.* **1987**, *122*, 242 (FIR LMR, $a^1\Delta$)		Ducas, T. W.; Geoffrion, L. D.; Osgood, R. M., Jr.; Javan, A. *Appl. Phys. Lett.* **1972**, *21*, 42 (laser osc.)
PH	Davies, P. B.; Russell, D. K.; Thrush, B. A. *Chem. Phys. Lett.* **1975**, *36*, 280 (FIR LMR)		Mizushima, M. *Phys. Rev.* **1972**, *A5*, 143 (LMR)
	Davies, P. B.; Russell, D. K.; Smith, D. R.; Thrush, B. A. *Can. J. Phys.* **1979**, *57*, 522 (FIR LMR, $a^1\Delta$)	(OD)	Meerts, W. L.; Dymanus, A. *Astrophys. J.* **1973**, *180*, L93 (MW)
			Ducas, T. W.; Javan, A. *J. Chem. Phys.* **1974**, *60*, 1677 (frequency measurements with MIM)
			Howard, C. J.; Evenson, K. M. *J. Chem. Phys.* **1974**, *61*, 1943 (FIR LMR, reaction)
(PD)	Uehara, H.; Hakuta, K. *J. Chem. Phys.* **1981**, *74*, 4326 (IR LMR)		Lee, K. P.; Tam, W. G. *Chem. Phys.* **1974**, *4*, 434 (EPR, excited vibrational states)
			Destombes, J. L.; Journel, G.; Marlière, C.; Rohart, M. *Compt. Rend.* **1975**, *280B*, 809 (MW, transient)
			Destombes, J. L.; Marlière, C. *Chem. Phys. Lett.* **1975**, *34*, 532 (MW–rf double resonance, hfs)

TABLE II (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
(OD)	Meerts, W. L.; Dymanus, A. *Can. J. Phys.* 1975, 53, 2123 (molecular beam electric resonance)	(OD)	Brown, J. M.; Schubert, J. E.; Brown, C. E.; Geiger, J. S.; Smith, D. R. *J. Mol. Spectrosc.* 1985, 114, 185; 1986, 116, 507 (FIR LMR, excited vibrational states)
	Howard, C. J.; Evenson, K. M. *J. Chem. Phys.* 1976, 64, 197 (FIR LMR, reaction)		
	ter Meulen, J. J.; Meerts, W. L.; van Mierls, G. W. M.; Dymanus, A. *Phys. Rev. Lett.* 1976, 36, 1031 (MW)		Blake, G. A.; Farhoomand, J.; Pickett, H. M. *J. Mol. Spectrosc.* 1986, 115, 226 (FIR laser sideband)
	Maillard, J. P.; Chauville, J.; Mantz, A. W. *J. Mol. Spectrosc.* 1976, 63, 120 (IR emission)	(^{18}OH)	Comben, E. R.; Brown, J. M.; Steimle, T. C.; Leopold, K. R.; Evenson, K. M. *Astrophys. J.* 1986, 305, 513 (MW, FIR LMR)
	Howard, C. J.; Evenson, K. M. *J. Chem. Phys.* 1976, 64, 4303 (FIR LMR, reaction)	(^{17}OH)	Leopold, K. R.; Evenson, K. M.; Comben, E. R.; Brown, J. M. *J. Mol. Spectrosc.* 1987, 122, 440 (FIR LMR, hfs)
	Howard, C. J. *J. Chem. Phys.* 1976, 65, 4771 (FIR LMR, reaction)		
	Bustreel, R.; Destombes, J. L.; Marlière, C. *Chem. Phys. Lett.* 1976, 42, 154 (MW, pressure broadening)		Brown, J. M.; Zink, L. R.; Jennings, D. A.; Evenson, K. M.; Hinz, A.; Nolt, I. G. *Astrophys. J.* 1986, 307, 410 (FIR)
(OD)	Rashid, M. H.; Lee, K. P.; Sastry, K. V. L. N. *J. Mol. Spectrosc.* 1977, 68, 299 (EPR)		Yaron, D.; Peterson, K.; Klemperer, W. *J. Chem. Phys.* 1988, 88, 4702 (mol beam, dipole moment)
	Brown, J. M.; Kaise, M.; Kerr, C. M. L.; Milton, D. J. *Mol. Phys.* 1978, 36, 553 (EPR, Zeeman)		Comben, E. R.; Brown, J. M. *Chem. Phys.* 1988, 119, 443 (analysis)
	Beaudet, R. A.; Poynter, R. L. *J. Phys. Chem. Ref. Data* 1978, 7, 311 (MW)		Nelson, Jr., D. D.; Schiffman, A.; Nesbitt, D. J.; Orlando, J. J.; Burkholder, J. B. *J. Chem. Phys.* 1990, 93, 7003 (FTIR and difference, dipole moment function)
	Meerts, W. L.; Bekooy, J. P.; Dymanus, A. *Mol. Phys.* 1979, 37, 425 (mol beam)		
	Lemoine, B.; Bustreel, R.; Demuynck-Marlière, C.; Destombes, J. L. *J. Chem. Phys.* 1979, 71, 3131 (MW, population inversion)		Chance, K. V.; Jennings, D. A.; Evenson, K. M.; Vanek, M. D.; Nolt, I. G.; Radostitz, J. V.; Park, K. *J. Mol. Spectrosc.* 1991, 146, 375 (tunable FIR, pressure broadening)
	Burrows, J. P.; Cliff, D. I.; Davies, P. B.; Harris, G. W.; Thrush, B. A.; Wilkinson, J. P. T. *Chem. Phys. Lett.* 1979, 65, 197 (FIR LMR, pressure broadening)		Benidar, A.; Guelachvili, G.; Martin, P. A. *Chem. Phys. Lett.* 1991, 177, 563 (FTIR, transient)
	Davies, P. B.; Hack, W.; Preuss, A. W.; Temps, F. *Chem. Phys. Lett.* 1979, 64, 94 (FIR LMR, excited vibrational states)		Hardwick, J. L.; Whipple, G. C. *J. Mol. Spectrosc.* 1991, 147, 267 (FIR emission)
	Destombes, J. L.; Lemoine, B.; Marlière-Demuynck, C. *Chem. Phys. Lett.* 1979, 60, 493 (MW, v=1)	SH (SD)	McDonald, C. C. *J. Chem. Phys.* 1963, 39, 2587 (EPR)
	Coxon, J. A.; Sastry, K. V. L. N.; Austin, J. A.; Levy, D. H. *Can. J. Phys.* 1979, 57, 619 (MW, excited vibrational states)		Radford, H. E.; Linzer, M. *Phys. Rev. Lett.* 1963, 10, 443 (EPR)
(OD)	Geiger, J. S.; Smith, D. R.; Bonnett, J. D. *Chem. Phys. Lett.* 1980, 70, 600 (FIR LMR)		Carrington, A.; Levy, D. H.; Miller, T. A. *J. Chem. Phys.* 1967, 47, 3801 (EPR)
			Uehara, H.; Morino, Y. *J. Mol. Spectrosc.* 1970, 36, 158 (EPR)
	Sastry, K. V. L. N.; Vanderlinde, J. *J. Mol. Spectrosc.* 1980, 83, 332 (MW, Zeeman)	(^{33}SH)	Miller, T. A. *J. Chem. Phys.* 1971, 54, 1658 (EPR)
	Brown, J. M.; Kerr, C. M. L.; Wayne, F. D.; Evenson, K. M.; Radford, H. E. *J. Mol. Spectrosc.* 1981, 86, 544 (FIR LMR)		Brown, J. M.; Thistlethwaite, P. J. *Mol. Phys.* 1972, 23, 635 (EPR)
			Tanimoto, M.; Uehara, H. *Mol. Phys.* 1973, 25, 1193 (EPR)
(OD)	Amiot, C.; Maillard, J.-P.; Chauville, J. *J. Mol. Spectrosc.* 1981, 87, 196 (FTIR)		Meerts, W. L.; Dymanus, A. *Astrophys. J.* 1974, 187, 45 (mol beam)
	Storey, J. W. V.; Watson, D. M.; Townes, C. H. *Astrophys. J.* 1981, 244, L27 (FIR astronomy)	(SD)	Meerts, W. L.; Dymanus, A. *Can. J. Phys.* 1975, 53, 2123 (mol beam electric resonance)
	Coxon, J. A.; Foster, S. C. *Can. J. Phys.* 1982, 60, 41 (IR emission)	(SD)	Davies, P. B.; Handy, B. J.; Murray Lloyd, E. K.; Russell, D. K. *Mol. Phys.* 1978, 36, 1005 (FIR LMR)
(OD)	Brown, J. M.; Schubert, J. E. *J. Mol. Spectrosc.* 1982, 95, 194 (EPR)	(SD)	Lowe, R. S. *Mol. Phys.* 1980, 41, 929 (IR LMR)
	Brown, J. M.; Schubert, J. E.; Evenson, K. M.; Radford, H. E. *Astrophys. J.* 1982, 258, 899 (FIR LMR)	(SD)	Rohrbeck, W.; Hinz, A.; Urban, W. *Mol. Phys.* 1980, 41, 925 (IR LMR)
	Geiger, J. S.; Smith, D. R.; Bonnett, J. D. *Chem. Phys.* 1983, 74, 239 (FIR LMR, transient)		Bernath, P. F.; Amano, T.; Wong, M. *J. Mol. Spectrosc.* 1983, 98, 20 (difference)
	Podolske, J. R.; Johnston, H. S. *J. Chem. Phys.* 1983, 79, 3633 (IR diode, line strength)		Winkel, R. J., Jr.; Davis, S. P. *Can. J. Phys.* 1984, 62, 1420 (IR LMR)
(OD)	Amano, T. *J. Mol. Spectrosc.* 1984, 103, 436 (difference)	(SD)	Zeitz, D.; Bohle, W.; Werner, J.; Hinz, A.; Urban, W. *Mol. Phys.* 1985, 54, 953 (IR LMR)
	Peterson, K. I.; Fraser, G. T.; Klemperer, W. *Can. J. Phys.* 1984, 62, 1502 (mol beam, dipole moment)		Benidar, A.; Farrenq, R.; Guelachvili, G.; Chackerian, C., Jr. *J. Mol. Spectrosc.* 1991, 147, 383 (FTIR, intensity)
	Farhoomand, J.; Blake, G. A.; Pickett, H. M. *Astrophys. J.* 1985, 291, L19 (FIR laser sideband)	SeH (SeD)	Carrington, A.; Currie, G. N.; Lucas, N. J. D. *Proc. R. Soc. Lond.* 1970, A315, 355 (EPR)
	Lemoine, B.; Bogey, M.; Destombes, J. L. *Chem. Phys. Lett.* 1985, 117, 532 (IR diode)		Davies, P. B.; Handy, B. J.; Murray Lloyd, E. K.; Russell, D. K. *J. Chem. Phys.* 1978, 68, 3377 (FIR LMR)
			Brown, J. M.; Carrington, A.; Sears, T. *J. Mol. Phys.* 1979, 37, 1837 (IR LMR)
	Van Herpen, W. M.; Meerts, W. L.; Veseth, L. *Chem. Phys. Lett.* 1985, 120, 247 (MW, Zeeman)	(SeD)	Brown, J. M.; Carrington, A.; Fackerell, A. D. *Chem. Phys. Lett.* 1981, 75, 13 (IR LMR)

TABLE II (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
(SeD)	Cliff, D. I.; Davies, P. B.; Handy, B. J.; Thrush, B. A.; Murray Lloyd, E. K. *Chem. Phys. Lett.* **1980**, *75*, 9 (FIR LMR) Ashworth, S. H.; Brown, J. M. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 1995 (IR, FIR LMR)	TeH(X²Π) (TeD)	Ashworth, S. H.; Brown, J. M. *Chem. Phys. Lett.* **1991**, *182*, 73 (IR LMR, μ from relative intensity) Towle, J. P.; Brown, J. M. *Mol. Phys.* **1991**, *74*, 465 (IR LMR)

[a] For abbreviations for the methods and others, see footnote a of Table I, in addition to the following: mol beam, molecular beam; hfs, hyperfine structure; FTIR, Fourier transform infrared; MODR, microwave–optical double resonance; Λ-doublet, Λ-type doublet; difference, difference frequency laser; MW, microwave; laser osc, laser oscillation; MIM, metal–insulator–metal device; and transient, time-resolved observation. [b] In cases where isotopic species are investigated (besides the parent species), these isotopic species are indicated in parentheses.

This phenomenon is referred to as Λ-type doubling, because the axial component of the orbital angular momentum is designated as Λ. As expected from the origin of this interaction, the expression for the interaction constant is quite similar to that of the spin–rotation interaction. Namely, for a Π state, the expression is given by

$$p = 2\sum(-1)^s\langle\Pi|A_{SO}L_+|\Sigma^s\rangle\langle\Sigma^s|BL_-|\Pi\rangle/[E(\Pi) - E(\Sigma)] \quad (2)$$

where s is 0 or 1 depending on whether the Σ state interacting with the Π state is Σ^+ or Σ^-, respectively, and $L_\pm = L_x \pm iL_y$. If the spin–orbit coupling constant A_{SO} and the rotational constant B are not much dependent on the electronic coordinate, they can be taken out from the matrix elements, leaving

$$\epsilon_{bb} = 4A_{SO}B\sum(-1)^{sn}|\langle0|L_b|n\rangle|^2/[E(n) - E(0)] \quad (3)$$

$$p = 2A_{SO}B\sum(-1)^s\langle\Pi|L_+|\Sigma^s\rangle\langle\Sigma^s|L_-|\Pi\rangle/[E(\Pi) - E(\Sigma)] \quad (4)$$

Although this approximation does not hold well in most cases, the constants still can be used to estimate the location of the excited state.

The expressions given above are derived by assuming that the electronic energy difference $E(n) - E(0)$ is much larger than the matrix elements. This assumption is quite good in many cases, but in a few instances there exist low-lying electronic states, which invalidate the above expressions for the constants. For example, Endo and Hirota[16] found anomalous spin–rotation splittings for the HCCO radical, namely the splittings of the $K_a = 2$ and 3 lines were much smaller than those expected from the $K_a = 1$ lines. The deviations were too large to be ascribed to centrifugal effects, and the observed splittings could be reproduced only by assuming a Padé-type expression for ϵ_{aa}:

$$\epsilon_{aa}(K) = \epsilon_{aa}/(1 + tK) \quad (5)$$

Endo and Hirota explained this anomaly by the presence of a low-lying excited electronic state. The HCCO molecule is isoelectronic with the linear molecule NCO, which has a ²Π ground electronic state. One may get the HCCO molecule by taking out a hydrogen from the nitrogen of NCO. If H–C–C is bent, the molecule will be subjected to the Renner–Teller effect, and the Π electronic state will be split into two, one of A' and the other of A" symmetry. Endo and Hirota determined the H–C–C angle to be 138.7°, and thus the upper state is expected to be very close to linear. Figure 1 shows a schematic diagram of energy levels in the ground and the excited electronic states; in the lower state the levels are rotational levels in the ground vibrational state,
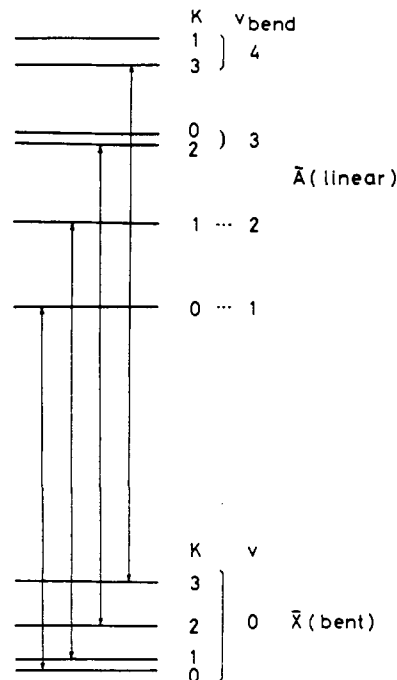

Figure 1. Schematic diagram for energy levels of the HCCO radical (reprinted from ref 16; copyright 1987 American Institute of Physics).

whereas the upper state consists of vibrational states of bending which are separated approximately by the bending frequency ω'. Here K denotes the quantum number of the angular momentum component along the molecular axis for both the bent and linear cases. As eq 3 shows, the interactions causing the ϵ_{aa} term obey the selection rule $\Delta K = 0$, and thus the energy difference in the denominator is given by $E_0 + \omega'K$, where E_0 denotes the electronic energy difference. The Padé-type expression, which is required to fit the observed data, can thus be explained if t is taken to be equal to ω'/E_0. The observed values of t for HCCO and DCCO are 0.564 93 and 0.247 25, which satisfy closely the ratio expected from the bending frequencies of the two isotopic species.

A simplified form of ϵ_{aa} derived from eq 3 is

$$\epsilon_{aa} = -4AA_{SO}/E_0 \quad (6)$$

If A_{SO} of the carbon atom (27.1 cm⁻¹) or of the oxygen atom (158.5 cm⁻¹) is used, the observed value of ϵ_{aa} gives E_0 to be 540 or 3200 cm⁻¹. This result is no more than qualitative or at best semiquantitative, but indicates that the excited state under consideration is very low, located somewhere in the infrared region.

A similar interesting case has recently been investigated by Miller and his co-workers,[17] namely the ethoxy

TABLE III. Diatomic Radicals[a]

species[b]	ref (method and comment)	species[b]	ref (method and comment)
1A-6B X^{2}Π		LaO	Törring, T.; Zimmermann, K.; Hoeft, J. Chem. Phys. Lett. 1988, 151, 520 (MW)
LiO	Berg, R. A.; Wharton, L.; Klemperer, W.; Büchler, A.; Stauffer, J. L. J. Chem. Phys. 1965, 43, 2416 (electric deflection)		Suenram, R. D.; Lovas, F. J.; Fraser, G. T.; Matsumura, K. J. Chem. Phys. 1990, 92, 4724 (MW)
	Freund, S. M.; Herbst, E.; Mariella, Jr., R. P.; Klemperer, W. J. Chem. Phys. 1972, 56, 1467 (mol beam, rf)	3B-6B X^{2}Σ$^+$	
		BO	Tanimoto, M.; Saito, S.; Hirota, E. J. Chem. Phys. 1986, 84, 1210 (MW)
	Yamada, C.; Fujitake, M.; Hirota, E. J. Chem. Phys. 1989, 91, 137 (MW)	BS	Tanimoto, M.; Saito, S.; Yamamoto, S. J. Chem. Phys. 1988, 88, 2296 (MW)
NaO	Yamada, C.; Fujitake, M.; Hirota, E. J. Chem. Phys. 1989, 90, 3033 (MW)	AlO	Törring, T.; Herrmann, R. Mol. Phys. 1989, 68, 1379 (MW, fs and hfs)
1B-6B X^{2}Π			Yamada, C.; Cohen, E. A.; Fujitake, M.; Hirota, E. J. Chem. Phys. 1990, 92, 2146 (MW)
CuO	Gerry, M. C. L.; Merer, A. J.; Sassenberg, U.; Steimle, T. C. J. Chem. Phys. 1987, 86, 4754 (MODR)	AlS	Takano, S.; Yamamoto, S.; Saito, S. J. Chem. Phys. 1991, 94, 3355 (mm wave)
2A-6B X^{2}Σ$^+$		3A-7B X^{1}Σ$^+$	
MgO	Civič, S.; Hedderich, H. G.; Blom, C. E. Chem. Phys. Lett. 1991, 176, 489 (IR diode)	YF	Shirley, J. E.; Barclay, Jr., W. L.; Ziurys, L. M.; Steimle, T. C. Chem. Phys. Lett. 1991, 183, 363 (mm wave ODR)
MgS	Takano, S.; Yamamoto, S.; Saito, S. Chem. Phys. Lett. 1989, 159, 563 (mm wave)	3B-7B X^{1}Σ$^+$	
CaO	Creswell, R. A.; Hocking, W. H.; Pearson, E. F. Chem. Phys. Lett. 1977, 48, 369 (mm wave)	BF	Lovas, F. J.; Johnson, D. R. J. Chem. Phys. 1971, 55, 41 (MW)
	Blom, C. E.; Hedderich, H. G. Chem. Phys. Lett. 1988, 145, 143 (IR diode)		Zahniser, M. S.; Gersh, M. E. J. Chem. Phys. 1981, 75, 52 (IR diode, intensity)
	Hedderich, H. G.; Blom, C. E. J. Chem. Phys. 1989, 90, 4660 (IR diode)		Nakanaga, T.; Takeo, H.; Kondo, S.; Matsumura, C. Chem. Phys. Lett. 1985, 113, 88 (IR diode)
CaS	Takano, S.; Yamamoto, S.; Saito, S. Chem. Phys. Lett. 1989, 159, 563 (mm wave)		Cazzoli, G.; Cludi, L.; Degli Esposti, C.; Dore, L. J. Mol. Spectrosc. 1989, 134, 159 (mm and submm wave)
BaO	Wharton, L.; Klemperer, W. J. Chem. Phys. 1963, 38, 2705 (MW)	BCl	Maki, A. G.; Lovas, F. J.; Suenram, R. D. J. Mol. Spectrosc. 1982, 91, 424 (IR diode)
	Brooks, R.; Kaufman, M. J. Chem. Phys. 1965, 43, 3406 (mol beam, Zeeman)		Endo, Y.; Saito, S.; Hirota, E. Bull. Chem. Soc. Jpn. 1983, 56, 3410 (MW, eQq)
	Hoeft, J.; Lovas, F. J.; Tiemann, E.; Törring, T. Z. Naturforsch. 1970, 25a, 1750 (MW)	GaF	Uehara, H.; Horiai, K.; Nakagawa, K.; Suguro, H. Chem. Phys. Lett. 1991, 178, 553 (FTIR)
	Tiemann, E.; Bojachewsky, M.; Sauter-Servaes, Ch.; Törring, T. Z. Naturforsch. 1974, 29a, 1692 (MW)	4B-4B	
		C$_2$	Yan, W.-B.; Curl, R. F.; Merer, A. J.; Carrick, P. G. J. Mol. Spectrosc. 1985, 112, 436 (color, electronic b^{3}Σ$_g$ ← a^{3}Π$_u$)
	Hedderich, H. G.; Blom, C. E. J. Mol. Spectrosc. 1990, 140, 103 (IR diode)	4B-4B X^{3}Π	
BaS	Merendres, C. A.; Hebert, A. J.; Street, Jr., K. J. Chem. Phys. 1969, 51, 855 (rf, dipole moment)	CSi	Cernicharo, J.; Gottlieb, C. A.; Guélin, M.; Thaddeus, P.; Vrtilek, J. M. Astrophys. J. 1989, 341, L25 (radioastronomy, mm wave)
	Helms, D. A.; Winnewisser, M.; Winnewisser, G. J. Phys. Chem. 1980, 84, 1758 (mm wave)	(isotopes)	Bogey, M.; Demuynck, C.; Destombes, J. L. Astron. Astrophys. 1990, 232, L19 (submm wave)
2A-7B X^{2}Σ$^+$		(^{13}CSi)	Mollaaghababa, R.; Gottlieb, C. A.; Vrtilek, J. M.; Thaddeus, P. Astrophys. J. 1990, 352, L21 (mm wave, excited vibrational state)
MgCl	Bogey, M.; Demuynck, C.; Destombes, J. L. Chem. Phys. Lett. 1989, 155, 265 (mm wave)	4B-5B X^{2}Σ$^+$	
CaCl, CaBr	Möller, K.; Schütze-Pahlmann, H.-U.; Hoeft, J.; Törring, T. Chem. Phys. 1982, 68, 399 (MW)	CN	Radford, H. E. Phys. Rev. 1964, 136, A1571 (MODR, B^{2}Σ$^+$)
CaI	Törring, T.; Doebl, K. Chem. Phys. Lett. 1985, 115, 328 (MW)		Wilson, R. W.; Solomon, P. M.; Penzias, A. A.; Jefferts, K. B. Astrophys. J. 1971, 169, L35 (radioastronomy)
SrF, SrCl	Schütze-Pahlmann, H.-U.; Ryzlewicz, Ch.; Hoeft, J.; Törring, T. Chem. Phys. Lett. 1982, 93, 74 (mm wave)		Penzias, A. A.; Wilson, R. W.; Jefferts, K. B. Phys. Rev. Lett. 1974, 32, 701 (radioastronomy, hfs)
SrBr, SrI	Törring, T.; Doebl, K.; Weiler, G. Chem. Phys. Lett. 1985, 117, 539 (MW)		Dixon, T. A.; Woods, R. C. J. Chem. Phys. 1977, 67, 3956 (MW)
BaF	Ryzlewicz, Ch.; Törring, T. Chem. Phys. 1980, 51, 329 (MW)		Davies, P. B.; Hamilton, P. A. J. Chem. Phys. 1982, 76, 2127 (IR diode)
	Ryzlewicz, Ch.; Schütze-Pahlmann, H.-U.; Hoeft, J.; Törring, T. Chem. Phys. 1982, 71, 389 (MW, hfs)		Skatrud, D. D.; De Lucia, F. C.; Blake, G. A.; Sastry, K. V. L. N. J. Mol. Spectrosc. 1983, 99, 35 (mm and submm wave, excited vibrational states)
	West, W. E.; Kändler, J.; Törring, T. J. Chem. Phys. 1986, 84, 4769 (MW, hfs and dipole moment)	(^{13}CN)	Bogey, M.; Demuynck, C.; Destombes, J. L. Can. J. Phys. 1984, 62, 1248 (mm wave)
BaCl	Ryzlewicz, Ch.; Schütze-Pahlmann, H.-U.; Hoeft, J.; Törring, T. Chem. Phys. 1982, 71, 389 (MW, hfs)	(^{13}CN)	Gerin, M.; Combes, F.; Encrenaz, P.; Linke, R.; Destombes, J. L.; Demuynck, C. Astron. Astrophys. 1984, 136, L17 (radioastronomy)
BaBr	West, W. E.; Weiler, G.; Törring, T. Chem. Phys. Lett. 1985, 121, 494 (MW, hfs)	(^{13}CN)	Bogey, M.; Demuynck, C.; Destombes, J. L. Chem. Phys. 1986, 102, 141 (mm wave, excited vibrational states)
BaI	Törring, T.; Döbl, K. Chem. Phys. Lett. 1985, 115, 328 (MW)		Balle, R. J.; Pasternack, L. J. Phys. Chem. 1987, 91, 73 (IR diode, reaction)
	Ernst, W. E.; Kändler, J.; Törring, T. Chem. Phys. Lett. 1986, 123, 243 (MW, dipole moment)	CP	Saito, S.; Yamamoto, S.; Kawaguchi, K.; Ohishi, M.; Suzuki, H.; Ishikawa, S.; Kaifu, N. Astrophys. J. 1989, 341, 1114 (MW)
3A-6B X^{2}Σ$^+$			
YO	Suenram, R. D.; Lovas, F. J.; Fraser, G. T.; Matsumura, K. J. Chem. Phys. 1990, 92, 4724 (MW)		
YS	Azuma, Y.; Childs, W. J. J. Chem. Phys. 1990, 93, 8415 (MODR, spin–rotation and hfs)		

TABLE III (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
	Guélin, M.; Cernicharo, J.; Paubert, G.; Turner, B. E. *Astron. Astrophys.* **1990**, *230*, L9 (radioastronomy)	CSe	McGurk, J.; Tigelaar, H. L.; Rock, S. L.; Norris, C. L.; Flygare, W. H. *J. Chem. Phys.* **1973**, *58*, 1420 (MW, dipole moment and Zeeman)
SiN	Saito, S.; Endo, Y.; Hirota, E. *J. Chem. Phys.* **1983**, *78*, 6447 (MW)	SiO, SiS	(not listed)
	Yamada, C.; Hirota, E. *J. Chem. Phys.* **1985**, *82*, 2547 (IR diode, A-X)	GeO	Törring, T. *Z. Naturforsch.* **1966**, *21a*, 287 (MW)
	Foster, S. C.; Lubic, K. G.; Amano, T. *J. Chem. Phys.* **1985**, *82*, 709 (difference, A-X)		Hoeft, J.; Lovas, F. J.; Tiemann, E.; Tischer, R.; Törring, T. *Z. Naturforsch.* **1969**, *24a*, 1217 (MW, dipole moment)
	Yamada, C.; Hirota, E.; Yamamoto, S.; Saito, S. *J. Chem. Phys.* **1988**, *88*, 46 (IR diode, A-X)		Raymonda, J. W.; Muenter, J. S.; Klemperer, W. A. *J. Chem. Phys.* **1970**, *52*, 3458 (mol beam, dipole moment)
4A-6B X¹Σ⁺			Hornerjäger, R.; Tischer, R. *Z. Naturforsch.* **1973**, *28a*, 1374 (MW, Zeeman)
ZrO, HfO	Suenram, R. D.; Lovas, F. J.; Fraser, G. T.; Matsumura, K. *J. Chem. Phys.* **1990**, *92*, 4724 (MW)		Davis, R. E.; Muenter, J. S. *J. Chem. Phys.* **1974**, *61*, 2940 (mol beam, Zeeman)
4B-6B ¹Σ⁺			Thompson, G. A.; Maki, A. G.; Weber, A. *J. Mol. Spectrosc.* **1986**, *116*, 136 (FTIR)
CS	Mockler, R. G.; Bird, G. R. *Phys. Rev.* **1955**, *98*, 1837 (MW)	GeS	Hoeft, J. *Z. Naturforsch.* **1965**, *20a*, 826 (MW)
	Kewley, R.; Sastry, K. V. L. N.; Winnewisser, M.; Gordy, W. *J. Chem. Phys.* **1963**, *39*, 2856 (MW)		Hoeft, J.; Lovas, F. J.; Tiemann, E.; Tischer, R.; Törring, T. *Z. Naturforsch.* **1969**, *24a*, 1217 (MW, dipole moment)
	Bates, H. E.; Gallagher, J. J.; Derr, V. E. *J. Appl. Phys.* **1968**, *39*, 3218 (mm wave)		Hoeft, J.; Lovas, F. J.; Tiemann, E.; Törring, T. *J. Chem. Phys.* **1970**, *53*, 2736 (MW, dipole moment and hfs)
	Winnewisser, G.; Cook, R. L. *J. Mol. Spectrosc.* **1968**, *28*, 266 (MW, dipole moment)		Le Floch, A. C.; Masson, J. *J. Mol. Spectrosc.* **1984**, *103*, 408 (MW, hfs)
	Gustafson, S.; Gordy, W. *J. Chem. Phys.* **1970**, *52*, 579 (MW, Zeeman)		Uehara, H.; Horiai, K.; Sueoka, K.; Nakagawa, K. *Chem. Phys. Lett.* **1989**, *160*, 149 (FTIR)
	Penzias, A. A.; Solomon, P. M.; Wilson, R. W.; Jefferts, K. B. *Astrophys. J.* **1971**, *168*, L53 (radioastronomy)	GeSe	Hoeft, J.; Lovas, F. J.; Tiemann, E.; Törring, T. *J. Chem. Phys.* **1970**, *53*, 2736 (MW, dipole moment and hfs)
	Wilson, R. W.; Solomon, P. M.; Penzias, A. A.; Jefferts, K. B. *Astrophys. J.* **1971**, *169*, L35 (radioastronomy)		Hoeft, J.; Lovas, F. J.; Tiemann, E.; Törring, T. *Z. Naturforsch.* **1970**, *25a*, 539 (MW, dipole moment)
	Zuckerman, B.; Morris, M.; Palmer, P.; Turner, B. E. *Astrophys. J.* **1972**, *173*, L125 (radioastronomy)	GeTe	Hoeft, J.; Nolting, H.-P. *Z. Naturforsch.* **1967**, *22a*, 1121 (MW)
	McGurk, J.; Tigelaar, H. L.; Rock, S. L.; Norris, C. L.; Flygare, W. H. *J. Chem. Phys.* **1973**, *58*, 1420 (MW, dipole moment)		Hoeft, J.; Lovas, F. J.; Tiemann, E.; Törring, T. *Z. Naturforsch.* **1970**, *25a*, 539 (MW, dipole moment)
	Wollrab, J. E.; Rasmussen, R. L. *J. Chem. Phys.* **1973**, *58*, 4702 (MW, lifetime)		Tiemann, E.; Hoeft, J.; Törring, T. *Z. Naturforsch.* **1971**, *26a*, 1930 (MW, hfs)
	Turner, B. E.; Zuckerman, B.; Palmer, P.; Morris, M. *Astrophys. J.* **1973**, *186*, 123 (radioastronomy)	SnS	Birk, H.; Jones, H. *Chem. Phys. Lett.* **1991**, *181*, 245 (IR diode)
	Destombes, J. L.; Marlière, C. *Compt. Rend.* **1973**, *277B*, 427 (MW, photolysis)	4B-7B X²Π	
	Lovas, F. J.; Krupenie, P. H. *J. Phys. Chem. Ref. Data* **1974**, *3*, 245 (MW)	CF	Carrington, A.; Howard, B. J. *Mol. Phys.* **1970**, *18*, 225 (EPR, dipole moment)
	Liszt, H. S.; Linke, R. A. *Astrophys. J.* **1975**, *196*, 709 (radioastronomy)		Kawaguchi, K.; Yamada, C.; Hamada, Y.; Hirota, E. *J. Mol. Spectrosc.* **1981**, *86*, 136 (IR diode)
	Wilson, R. W.; Penzias, A. A.; Wannier, P. G.; Linke, R. A. *Astrophys. J.* **1976**, *204*, L135 (radioastronomy)		Van den Heuvel, F. C.; Meerts, W. L.; Dymanus, A. *Chem. Phys. Lett.* **1982**, *88*, 59 (FIR)
	Todd, T. R. *J. Mol. Spectrosc.* **1977**, *66*, 162 (IR diode)		Saykally, R. J.; Lubic, K. G.; Scalabrin, A.; Evenson, K. M. *J. Chem. Phys.* **1982**, *77*, 58 (FIR LMR)
(isotopes)	Todd, T. R.; Olson, W. B. *J. Mol. Spectrosc.* **1979**, *74*, 190 (IR diode)		Saito, S.; Endo, Y.; Takami, M.; Hirota, E. *J. Chem. Phys.* **1983**, *78*, 116 (MW)
	Yamada, C.; Hirota, E. *J. Mol. Spectrosc.* **1979**, *74*, 203 (IR diode)		Gondal, M. A.; Rohrbeck, W.; Urban, W.; Blanckart, R.; Brown, J. M. *J. Mol. Spectrosc.* **1983**, *100*, 290 (IR LMR)
	Bustreel, R.; Demuynck-Marlière, C.; Destombes, J. L.; Journel, G. *Chem. Phys. Lett.* **1979**, *67*, 178 (MW, high v)		Brown, J. M.; Schubert, J. E.; Saykally, R. J.; Evenson, K. M. *J. Mol. Spectrosc.* **1986**, *120*, 421 (FIR LMR)
(isotopes)	Bogey, M.; Demuynck, C.; Destombes, J. L. *Chem. Phys. Lett.* **1981**, *81*, 256 (mm wave)	CCl	Yamada, C.; Nagai, K.; Hirota, E. *J. Mol. Spectrosc.* **1981**, *85*, 416 (IR diode)
	Bogey, M.; Demuynck, C.; Destombes, J. L. *J. Mol. Spectrosc.* **1982**, *95*, 35 (mm and submm wave, excited vibrational states)		Endo, Y.; Saito, S.; Hirota, E. *J. Mol. Spectrosc.* **1982**, *94*, 199 (MW)
	Winkel, Jr., R. J.; Davis, S. P.; Pecyner, R.; Brault, J. W. *Can. J. Phys.* **1984**, *62*, 1414 (FTIR)		Burkholder, J. B.; Sinha, A.; Hammer, P. D.; Howard, C. J. *J. Mol. Spectrosc.* **1988**, *127*, 61 (FTIR)
	Kolbe, W. F.; Leskovar, B. *J. Chem. Phys.* **1986**, *85*, 7117 (mm wave, transient)	SiF	Tanimoto, M.; Saito, S.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1983**, *100*, 205 (MW)
	Kanamori, H.; Hirota, E. *J. Chem. Phys.* **1987**, *86*, 3901 (IR diode, transient)		Tanaka, K.; Akiyama, Y.; Tanaka, T. *J. Mol. Spectrosc.* **1989**, *137*, 55 (IR diode)
	Burkholder, J. B.; Lovejoy, E. R.; Hammer, P. D.; Howard, C. J. *J. Mol. Spectrosc.* **1987**, *124*, 450 (FTIR)	SiCl	Tanimoto, M.; Saito, S.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1984**, *103*, 330 (MW)
	Lopez Piñeiro, A.; Tipping, R. H.; Chackerian, C., Jr. *J. Mol. Spectrosc.* **1987**, *125*, 91 (calc of intensity)	GeF	Tanimoto, M.; Saito, S.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *116*, 499 (MW)

TABLE III (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
5A-6B X⁴Σ⁻		BiF	Fink, E. H.; Setzer, K. D.; Ramsay, D. A.; Vervloet, M. *Chem. Phys. Lett.* **1991**, *179*, 95 (FTIR)
VO	Suenram, R. D.; Fraser, G. T.; Lovas, F. J.; Gillies, C. W. *J. Mol. Spectrosc.* **1991**, *148*, 114 (MW, μ)	BiI	Tischer, R.; Möller, K.; Törring, T. *Chem. Phys.* **1981**, *62*, 115 (MW, hfs)
NbO	Suenram, R. D.; Fraser, G. T.; Lovas, F. J.; Gillies, C. W. *J. Mol. Spectrosc.* **1991**, *148*, 114 (MW, μ)	**6B-6B X³Σ⁻**	
5B-6B X²Π		S₂	Wayne, F. D.; Davies, P. B.; Thrush, B. A. *Mol. Phys.* **1974**, *28*, 989 (EPR)
NS	Carrington, A.; Levy, D. H. *J. Phys. Chem.* **1967**, *71*, 2 (EPR)		Picket, H. M.; Boyd, T. L. *J. Mol. Spectrosc.* **1979**, *75*, 53 (mm wave)
	Carrington, A.; Howard, B. J.; Levy, D. H.; Robertson, J. C. *Mol. Phys.* **1968**, *15*, 187 (EPR)	SO	McDonald, C. C. *J. Chem. Phys.* **1963**, *39*, 2587 (EPR)
	Amano, T.; Saito, S.; Hirota, E.; Morino, Y. *J. Mol. Spectrosc.* **1969**, *32*, 97 (MW)		Powell, F. X.; Lide, D. R., Jr. *J. Chem. Phys.* **1964**, *41*, 1413 (MW)
	Uehara, H.; Morino, Y. *Mol. Phys.* **1969**, *17*, 239 (EPR)		Winnewisser, M.; Sastry, K. V. L. N.; Cook, R. L.; Gordy, W. *J. Chem. Phys.* **1964**, *41*, 1687 (mm wave)
	Byfleet, C. R.; Carrington, A.; Russell, D. K. *Mol. Phys.* **1971**, *20*, 271 (EPR, dipole moment)		Carrington, A.; Levy, D. H.; Miller, T. A. *Proc. R. Soc. Lond.* **1966**, *A293*, 108 (EPR, a¹Δ)
	Marlière, C.; Burie, J.; Destombes, J.-L. *Compt. Rend.* **1972**, *275B*, 315 (MW)		Daniels, J. M.; Dorain, P. B. *J. Chem. Phys.* **1966**, *45*, 26 (EPR)
	Matsumura, K.; Kawaguchi, K.; Nagai, K.; Yamada, C.; Hirota, E. *J. Mol. Spectrosc.* **1980**, *84*, 68 (IR diode)		Carrington, A.; Levy, D. H.; Miller, T. A. *J. Chem. Phys.* **1967**, *47*, 3801 (EPR)
	Lovas, F. J.; Suenram, R. D. *J. Mol. Spectrosc.* **1982**, *93*, 416 (MW)		Carrington, A.; Levy, D. H. *J. Phys. Chem.* **1967**, *71*, 2 (EPR)
	Anacona, J. R.; Bogey, M.; Davies, P. B.; Demuynck, C.; Destombes, J. L. *Mol. Phys.* **1986**, *59*, 81 (mm wave)		Amano, T.; Hirota, E.; Morino, Y. *J. Phys. Soc. Jpn.* **1967**, *22*, 399; **1968**, *25*, 300 (MW, eQq and hfs)
	Sinha, A.; Burkholder, J. B.; Hammer, P. D.; Howard, C. J. *J. Mol. Spectrosc.* **1988**, *130*, 466 (FTIR)	(³³SO)	Carrington, A.; Levy, D. H.; Miller, T. A. *Mol. Phys.* **1967**, *13*, 401 (EPR, hfs)
NSe	Brown, J. M.; Uehara, H. *J. Chem. Phys.* **1987**, *87*, 880 (IR LMR)		Carrington, A.; Levy, D. H.; Miller, T. A. *Proc. R. Soc. Lond.* **1967**, *A298*, 340 (EPR)
PO	Kawaguchi, K.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1983**, *79*, 629 (FIR LMR, MW)		Solomon, J. E.; Johnson, D. R.; Lin, C. C. *J. Mol. Spectrosc.* **1968**, *27*, 517 (MW, Zeeman)
	Butler, J. E.; Kawaguchi, K.; Hirota, E. *J. Mol. Spectrosc.* **1983**, *101*, 161 (IR diode)		Uehara, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 886 (EPR)
	Kanata, H.; Yamamoto, S.; Saito, S. *J. Mol. Spectrosc.* **1988**, *131*, 89 (MW, dipole moment)		Saito, S. *J. Chem. Phys.* **1970**, *53*, 2544 (MW, a¹Δ)
PS	Kawaguchi, K.; Hirota, E.; Ohishi, M.; Suzuki, H.; Takano, S.; Yamamoto, S.; Saito, S. *J. Mol. Spectrosc.* **1988**, *130*, 81 (IR diode)		Uehara, H.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2273 (EPR, a¹Δ)
	Ohishi, M.; Yamamoto, S.; Saito, S.; Kawaguchi, K.; Suzuki, H.; Kaifu, N.; Ishikawa, S.; Takano, S.; Tsuji, T.; Unno, W. *Astrophys. J.* **1988**, *329*, 511 (MW)		Byfleet, C. R.; Carrington, A.; Russell, D. K. *Mol. Phys.* **1971**, *20*, 271 (EPR, dipole moment)
AsO	Uehara, H. *Chem. Phys. Lett.* **1981**, *84*, 539 (IR LMR)		Uehara, H. *Mol. Phys.* **1971**, *21*, 407 (EPR, a¹Δ)
BiO	Fink, E. H.; Setzer, K. D.; Ramsay, D. A.; Vervloet, M. *Chem. Phys. Lett.* **1991**, *179*, 103 (FTIR)		Miller, T. A. *J. Chem. Phys.* **1971**, *54*, 1658 (EPR, a¹Δ, eQq)
5B-7B X³Σ⁻			Cupitt, L. T.; Glass, G. P. *Trans. Faraday Soc.* **1971**, *67*, 1 (EPR)
NF	Curran, A. H.; MacDonald, R. G.; Stone, A. J.; Thrush, B. A. *Chem. Phys. Lett.* **1971**, *8*, 451 (EPR, a¹Δ)		Breckenridge, W. H.; Miller, T. A. *J. Chem. Phys.* **1972**, *56*, 465 (EPR, reaction)
	Davies, P. B.; Hamilton, P. A.; Okumura, M. *J. Chem. Phys.* **1981**, *75*, 4294 (IR diode, a¹Δ)		Breckenridge, W. H.; Miller, T. A. *J. Chem. Phys.* **1972**, *56*, 475 (EPR)
	Davies, P. B.; Temps, F. *J. Chem. Phys.* **1981**, *74*, 6556 (FIR LMR, a¹Δ)		Marlière, C.; Burie, J.; Destombes, J.-L. *Compt. Rend.* **1972**, *275B*, 315 (MW)
	Davies, P. B.; Rothwell, W. J. *Proc. R. Soc. Lond.* **1983**, *A389*, 205 (IR diode)		Destombes, J. L.; Marlière, C. *Compt. Rend.* **1973**, *277B*, 427 (MW, photolysis)
	Davies, P. B.; Ferguson, A. H.; Stern, D. P.; Temps, F. *J. Mol. Spectrosc.* **1985**, *113*, 28 (FIR LMR, a¹Δ)		Gottlieb, C. A.; Ball, J. A. *Astrophys. J.* **1974**, *184*, L59; **1974**, *187*, L47 (radioastronomy)
	Yamamoto, S.; Saito, S. *J. Chem. Phys.* **1987**, *86*, 102 (MW, a¹Δ)	(isotopes)	Tiemann, E. *J. Mol. Spectrosc.* **1974**, *51*, 316 (MW)
NCl	Yamada, C.; Endo, Y.; Hirota, E. *J. Chem. Phys.* **1983**, *79*, 4159 (MW)		Tiemann, E. *J. Phys. Chem. Ref. Data* **1974**, *3*, 259 (MW)
(isotopes)	Yamada, C.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *115*, 105 (IR diode, mm wave)		Veseth, L.; Loftus, A. *Mol. Phys.* **1974**, *27*, 511 (MW)
(¹⁵NCl)	Yamada, C.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *117*, 134 (submm wave)		Davies, P. B.; Wayne, F. D.; Stone, A. J. *Mol. Phys.* **1974**, *28*, 1409 (EPR, excited vibrational states)
PF	Saito, S.; Endo, Y.; Hirota, E. *J. Chem. Phys.* **1985**, *82*, 2947 (MW)		Clark, W. W.; De Lucia, F. C. *J. Mol. Spectrosc.* **1976**, *60*, 332 (MW, a¹Δ)
	Yamada, C.; Chang, M. C.; Hirota, E. *J. Chem. Phys.* **1987**, *86*, 3804 (IR diode)		Yamada, C.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1978**, *69*, 1942 (IR LMR, a¹Δ)
PCl	Minowa, T.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1985**, *83*, 4939 (MW)		Kawaguchi, K.; Yamada, C.; Hirota, E. *J. Chem. Phys.* **1979**, *71*, 3338 (IR LMR)
	Kanamori, H.; Yamada, C.; Butler, J. E.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1985**, *83*, 4945 (IR diode)		Bogey, M.; Demuynck, C.; Destombes, J. L. *Chem. Phys.* **1982**, *66*, 99 (mm wave, excited vibrational states)
		(isotopes)	Tiemann, E. *J. Mol. Spectrosc.* **1982**, *91*, 60 (MW)
			Wong, M.; Amano, T.; Bernath, P. F. *J. Chem. Phys.* **1982**, *77*, 2211 (difference, v=3-0)
			Kanamori, H.; Butler, J. E.; Kawaguchi, K.; Yamada, C.; Hirota, E. *J. Mol. Spectrosc.* **1985**, *113*, 262 (IR diode, transient)

TABLE III (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
	Kanamori, H.; Butler, J. E.; Kawaguchi, K.; Yamada, C.; Hirota, E. *J. Chem. Phys.* **1985**, *83*, 611 (IR diode, transient)		Lee, Y.-P.; Stimpfle, R. M.; Perry, R. A.; Mucha, J. A.; Evenson, K. M.; Jennings, D. A.; Howard, C. J. *Int. J. Chem. Kinet.* **1982**, *14*, 711 (FIR LMR, reaction)
	Kolbe, W. F.; Leskovar, B. *Rev. Sci. Instrum.* **1985**, *56*, 1577 (mm wave, transient)		Cohen, E. A.; Pickett, H. M.; Geller, M. *J. Mol. Spectrosc.* **1984**, *106*, 430 (submm wave)
	Kolbe, W. F.; Leskovar, B. *J. Chem. Phys.* **1986**, *85*, 7117 (mm wave, transient)		Burkholder, J. B.; Hammer, P. D.; Howard, C. J.; Maki, A. G.; Thompson, G.; Chackerian, Jr., C. *J. Mol. Spectrosc.* **1987**, *124*, 139 (FTIR)
	Burkholder, J. B.; Lovejoy, E. R.; Hammer, P. D.; Howard, C. J.; Mizushima, M. *J. Mol. Spectrosc.* **1987**, *124*, 379 (FTIR, a$^1\Delta$)		Lang, V. I.; Sander, S. P.; Freidl, R. R. *J. Mol. Spectrosc.* **1988**, *132*, 89 (FTIR, intensity)
	Endo, Y.; Kanamori, H.; Hirota, E. *Chem. Phys. Lett.* **1987**, *141*, 129 (submm wave, a$^1\Delta$, transient)		Yaron, D.; Peterson, K.; Klemperer, W. *J. Chem. Phys.* **1988**, *88*, 4702 (mol beam, dipole moment)
	Kanamori, H.; Tiemann, E.; Hirota, E. *J. Chem. Phys.* **1988**, *89*, 621 (IR diode, a$^1\Delta$, transient)	OBr	Carrington, A.; Levy, D. H.; Miller, T. A. *J. Chem. Phys.* **1967**, *47*, 3801 (EPR)
SeO	Carrington, A.; Currie, G. N.; Dyer, P. N.; Levy, D. H.; Miller, T. A. *Chem. Commun.* **1967**, 641 (EPR)		Carrington, A.; Levy, D. H. *J. Phys. Chem.* **1967**, *71*, 2 (EPR)
	Carrington, A.; Levy, D. H. *J. Phys. Chem.* **1967**, *71*, 2 (EPR)		Powell, F. X.; Johnson, D. R. *J. Chem. Phys.* **1969**, *50*, 4596 (MW)
	Carrington, A.; Currie, G. N.; Levy, D. H.; Miller, T. A. *Mol. Phys.* **1969**, *17*, 535 (EPR, a$^1\Delta$)		Carrington, A.; Dyer, P. N.; Levy, D. H. *J. Chem. Phys.* **1970**, *52*, 309 (EPR)
	Byfleet, C. R.; Carrington, A.; Russell, D. K. *Mol. Phys.* **1971**, *20*, 271 (EPR, dipole moment)		Brown, J. M.; Byfleet, C. R.; Howard, B. J.; Russell, D. K. *Mol. Phys.* **1972**, *23*, 457 (EPR)
	Brown, J. M.; Dumper, K.; Parent, C. R. *Mol. Phys.* **1978**, *36*, 1149 (EPR)		Amano, T.; Yoshinaga, A.; Hirota, E. *J. Mol. Spectrosc.* **1972**, *44*, 594 (MW)
	Parent, C. R.; Kuijpers, P. J. M. *Chem. Phys.* **1979**, *40*, 425 (mm wave)		McKellar, A. R. W. *J. Mol. Spectrosc.* **1981**, *86*, 43 (IR LMR, $^2\Pi_{1/2}$–$^2\Pi_{3/2}$)
	Hakuta, K.; Uehara, H. *J. Mol. Spectrosc.* **1981**, *85*, 97 (IR LMR)		Cohen, E. A.; Pickett, H. M.; Geller, M. *J. Mol. Spectrosc.* **1981**, *87*, 459 (MW)
6B-7B X$^2\Pi$			Butler, J. E.; Kawaguchi, K.; Hirota, E. *J. Mol. Spectrosc.* **1984**, *104*, 372 (IR diode)
OF	McKellar, A. R. W. *Can. J. Phys.* **1979**, *57*, 2106 (IR LMR)		Orlando, J. J.; Burkholder, J. B.; Bopegedera, A. M. R. P.; Howard, C. J. *J. Mol. Spectrosc.* **1991**, *145*, 278 (FTIR)
	McKellar, A. R. W.; Yamada, C.; Hirota, E. *J. Mol. Spectrosc.* **1983**, *97*, 425 (IR diode)	OI	Carrington, A.; Currie, G. N.; Dyer, P. N.; Levy, D. H.; Miller, T. A. *J. Chem. Soc., Chem. Commun.* **1967**, 641 (EPR)
	McKellar, A. R. W. *J. Mol. Spectrosc.* **1983**, *101*, 186 (IR LMR, dipole moment)		Carrington, A.; Dyer, P. N.; Levy, D. H. *J. Chem. Phys.* **1970**, *52*, 309 (EPR)
	Burkholder, J. B.; Hammer, P. D.; Howard, C. J.; McKellar, A. R. W. *J. Mol. Spectrosc.* **1986**, *118*, 471 (FTIR)		Byfleet, C. R.; Carrington, A.; Russell, D. K. *Mol. Phys.* **1971**, *20*, 271 (EPR, dipole moment)
	Hammer, P. D.; Sinha, A.; Burkholder, J. B.; Howard, C. J. *J. Mol. Spectrosc.* **1988**, *129*, 99 (IR chemiluminescence)		Brown, J. M.; Byfleet, C. R.; Howard, B. J.; Russell, D. K. *Mol. Phys.* **1972**, *23*, 457 (EPR)
OCl	Carrington, A.; Dyer, P. N.; Levy, D. H. *J. Chem. Phys.* **1967**, *47*, 1756 (EPR)		Saito, S. *J. Mol. Spectrosc.* **1973**, *48*, 530 (MW)
	Carrington, A.; Levy, D. H.; Miller, T. A. *J. Chem. Phys.* **1967**, *47*, 3801 (EPR, dipole moment)	SF	Carrington, A.; Currie, G. N.; Miller, T. A.; Levy, D. H. *J. Chem. Phys.* **1969**, *50*, 2726 (EPR)
	Carrington, A.; Levy, D. H. *J. Phys. Chem.* **1967**, *71*, 2 (EPR)		Byfleet, C. R.; Carrington, A.; Russell, D. K. *Mol. Phys.* **1971**, *20*, 271 (EPR, dipole moment)
	Amano, T.; Hirota, E.; Morino, Y. *J. Mol. Spectrosc.* **1968**, *27*, 257 (MW)		Amano, T.; Hirota, E. *J. Mol. Spectrosc.* **1973**, *45*, 417 (MW)
	Amano, T.; Saito, S.; Hirota, E.; Morino, Y.; Johnson, D. R.; Powell, F. X. *J. Mol. Spectrosc.* **1969**, *30*, 275 (MW)		Endo, Y.; Saito, S.; Hirota, E. *J. Mol. Spectrosc.* **1982**, *92*, 443 (MW)
	Uehara, H.; Morino, Y. *J. Mol. Spectrosc.* **1970**, *36*, 158 (EPR)		Endo, Y.; Nagai, K.; Yamada, C.; Hirota, E. *J. Mol. Spectrosc.* **1983**, *97*, 213 (IR diode)
	Uehara, H.; Tanimoto, M.; Morino, Y. *Mol. Phys.* **1971**, *22*, 799 (EPR, hfs)	SCl	Yamada, C.; Butler, J. E.; Kawaguchi, K.; Kanamori, H.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *116*, 108 (IR diode)
	Amano, T.; Hirota, E. *J. Mol. Spectrosc.* **1977**, *66*, 185 (MW, excited vibrational state)		Tiemann, E.; Kanamori, H.; Hirota, E. *J. Mol. Spectrosc.* **1989**, *137*, 278 (IR diode, transient)
	Menzies, R. T.; Margolis, J. S.; Hinkley, E. D.; Toth, R. A. *Appl. Opt.* **1977**, *16*, 523 (IR diode)	SeF	Carrington, A.; Currie, G. N.; Miller, T. A.; Levy, D. H. *J. Chem. Phys.* **1969**, *50*, 2726 (EPR)
	Rogowski, R. S.; Bair, C. H.; Wade, W. R.; Hoell, J. M.; Copeland, G. E. *Appl. Opt.* **1978**, *17*, 1301 (IR diode)		Byfleet, C. R.; Carrington, A.; Russell, D. K. *Mol. Phys.* **1971**, *20*, 271 (EPR, dipole moment)
	Kakar, R. K.; Cohen, E. A.; Geller, M. *J. Mol. Spectrosc.* **1978**, *70*, 243 (MW)		Brown, J. M.; Byfleet, C. R.; Howard, B. J.; Russell, D. K. *Mol. Phys.* **1972**, *23*, 457 (EPR)
	Stimpfle, R. M.; Perry, R. A.; Howard, C. J. *J. Chem. Phys.* **1979**, *71*, 5183 (FIR LMR, reaction)	8-6B	
	Lowe, R. S.; McKellar, A. R. W. *J. Mol. Spectrosc.* **1980**, *79*, 424 (IR LMR, v=2–0)	FeO	DeVore, T. C.; Gallagher, T. N. *J. Chem. Phys.* **1979**, *70*, 4429 (IR, X$^5\Delta$)
	Maki, A. G.; Lovas, F. J.; Olson, W. B. *J. Mol. Spectrosc.* **1982**, *92*, 410 (IR diode, heterodyne)		Endo, Y.; Saito, S.; Hirota, E. *Astrophys. J.* **1984**, *278*, L131 (mm wave)
		CoO	DeVore, T. C.; Gallagher, T. N. *J. Chem. Phys.* **1979**, *71*, 474 (IR)

TABLE IV. Linear Radicals[a]

species[b]	ref (method and comment)	species[b]	ref (method and comment)
CCH	Tucker, K. D.; Kutner, M. L.; Thaddeus, P. *Astrophys. J.* 1974, *193*, L115 (radioastronomy)	(C₃D)	Yamamoto, S.; Saito, S.; Suzuki, H.; Deguchi, S.; Kaifu, N.; Ishikawa, S.; Ohishi, M. *Astrophys. J.* 1990, *348*, 363 (MW, radioastronomy)
	Sastry, K. V. L. N.; Helminger, P.; Charo, A.; Herbst, E.; De Lucia, F. C. *Astrophys. J.* 1981, *251*, L119 (mm and submm wave)	C₄H	Irvine, W. M.; Höglund, B.; Friberg, P.; Askne, J.; Elldér, J. *Astrophys. J.* 1981, *248*, L113 (radioastronomy)
	Ziurys, L. M.; Saykally, R. J.; Plambeck, R. L.; Erickson, N. R. *Astrophys. J.* 1982, *254*, 94 (radioastronomy)		Bell, M. B.; Sears, T. J.; Matthews, H. E. *Astrophys. J.* 1982, *255*, L75 (radioastronomy)
	Carrick, P. G.; Pfeiffer, J.; Curl, Jr., R. F.; Koester, E.; Tittel, F. K.; Kasper, J. V. V. *J. Chem. Phys.* 1982, *76*, 3336 (color, Å–X̃)		Gottlieb, C. A.; Gottlieb, E. W.; Thaddeus, P.; Kawamura, H. *Astrophys. J.* 1983, *275*, 916 (mm wave)
	Gottlieb, C. A.; Gottlieb, E. W.; Thaddeus, P. *Astrophys. J.* 1983, *264*, 740 (mm wave, radioastronomy)		Yamamoto, S.; Saito, S.; Guélin, M.; Cernicharo, J.; Suzuki, H.; Ohishi, M. *Astrophys. J.* 1987, *323*, L149 (MW, radioastronomy, excited vibrational states)
	Carrick, P. G.; Merer, A. J.; Curl, Jr., R. F. *J. Chem. Phys.* 1983, *78*, 3652 (color, Å–X̃)		Guélin, M.; Cernicharo, J.; Navarro, S.; Woodward, D. R.; Gottlieb, C. A.; Thaddeus, P. *Astron. Astrophys.* 1987, *182*, L37 (radioastronomy, excited vibrational states)
	Saykally, R. J.; Veseth, L.; Evenson, K. M. *J. Chem. Phys.* 1984, *80*, 2247 (FIR LMR)	(C₄D)	Woodward, D. R.; Pearson, J. C.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J.* 1988, *333*, L29 (mm wave)
	Curl, Jr., R. F.; Carrick, P. G.; Merer, A. J. *J. Chem. Phys.* 1985, *82*, 3479; 1985, *83*, 4278 (color, Å–X̃)	C₅H	Gottlieb, C. A.; Gottlieb, E. W.; Thaddeus, P. *Astron. Astrophys.* 1986, *164*, L5 (mm wave)
(CCD)	Vrtilek, J. M.; Gottlieb, C. A.; Langer, W. D.; Thaddeus, P.; Wilson, R. W. *Astrophys. J.* 1985, *296*, L35 (mm wave, radioastronomy)		Cernicharo, J.; Kahane, C.; Gomez-Gonzalez, J.; Guélin, M. *Astron. Astrophys.* 1986, *167*, L5 (radioastronomy)
(CCD)	Bogey, M.; Demuynck, C.; Destombes, J. L. *Astron. Astrophys.* 1985, *144*, L15 (mm and submm wave)		Cernicharo, J.; Guélin, M.; Walmsley, C. M. *Astron. Astrophys.* 1987, *172*, L5 (radioastronomy, hfs)
(CCD)	Combes, F.; Boulanger, F.; Encrenaz, P. J.; Gerin, M.; Bogey, M.; Demuynck, C.; Destombes, J. L. *Astron. Astrophys.* 1985, *147*, L25 (radioastronomy)	C₆H	Suzuki, H.; Ohishi, M.; Kaifu, N.; Ishikawa, S.; Kasuga, T.; Saito, S.; Kawaguchi, K. *Publ. Astron. Soc. Jpn.* 1986, *38*, 911 (radioastronomy)
	Yan, W.-B.; Hall, J. L.; Stephens, J. W.; Richnow, M. L.; Curl, R. F. *J. Chem. Phys.* 1987, *86*, 1657 (color, excited vibrational states)		Saito, S.; Kawaguchi, K.; Suzuki, H.; Ohishi, M.; Kaifu, N.; Ishikawa, S. *Publ. Astron. Soc. Jpn.* 1987, *39*, 193 (radioastronomy)
	Kanamori, H.; Seki, K.; Hirota, E. *J. Chem. Phys.* 1987, *87*, 73 (IR diode, ν₃ transient)		Pearson, J. C.; Gottlieb, C. A.; Woodward, D. R.; Thaddeus, P. *Astron. Astrophys.* 1988, *189*, L13 (mm wave)
(CCD)	Yan, W.-B.; Dane, C. B.; Zeitz, D.; Hall, J. L.; Curl, R. F. *J. Mol. Spectrosc.* 1987, *123*, 486 (color)	HNSi	Elhanine, M.; Farrenq, R.; Guelachvili, G. *J. Chem. Phys.* 1991, *94*, 2529 (FTIR, ν₁)
	Woodward, D. R.; Pearson, J. C.; Gottlieb, C. A.; Guélin, M.; Thaddeus, P. *Astron. Astrophys.* 1987, *186*, L14 (mm wave, excited vibrational states)		Bogey, M.; Demuynck, C.; Destombes, J. L.; Walters, A. *Astron. Astrophys.* 1991, *244*, L47 (mm and submm wave)
	Vervloet, M.; Herman, M. *Chem. Phys. Lett.* 1988, *144*, 48 (FT emission)	BO₂	Kawaguchi, K.; Hirota, E.; Yamada, C. *Mol. Phys.* 1981, *44*, 509 (IR diode)
	Kawaguchi, K.; Amano, T.; Hirota, E. *J. Mol. Spectrosc.* 1988, *131*, 58 (IR diode, ν₂ + ν₃)		Kawaguchi, K.; Hirota, E. *J. Mol. Spectrosc.* 1986, *116*, 450 (IR diode)
	Brown, J. M.; Evenson, K. M. *J. Mol. Spectrosc.* 1988, *131*, 161 (FIR LMR, excited vibrational states)		Maki, A. G.; Burkholder, J. B.; Sinha, A.; Howard, C. J. *J. Mol. Spectrosc.* 1988, *130*, 238 (FTIR)
	Kanamori, H.; Hirota, E. *J. Chem. Phys.* 1988, *89*, 3962 (IR diode)	HBO	Kawashima, Y.; Kawaguchi, K.; Hirota, E. *Chem. Phys. Lett.* 1986, *131*, 205 (IR diode)
	Keady, J. J.; Hinkle, K. H. *Astrophys. J.* 1988, *331*, 539 (IR astronomy)		Kawashima, Y.; Endo, Y.; Kawaguchi, K.; Hirota, E. *Chem. Phys. Lett.* 1987, *135*, 441 (MW)
(CCD)	Kanamori, H.; Hirota, E. *J. Chem. Phys.* 1988, *88*, 6699 (IR diode)		Kawashima, Y.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* 1989, *133*, 116 (MW)
(CCD)	Stephens, J. W.; Yan, W.-B.; Richnow, M. L.; Solka, H.; Curl, R. F. *J. Mol. Struct.* 1988, *190*, 41 (color)	FBO	Kawashima, Y.; Kawaguchi, K.; Endo, Y.; Hirota, E. *J. Chem. Phys.* 1987, *87*, 2006 (IR diode, MW)
(CCD)	Endo, Y.; Kanamori, H.; Hirota, E. *Chem. Phys. Lett.* 1989, *160*, 280 (mm and submm wave, excited vibrational states)	ClBO	Kawaguchi, K.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* 1982, *93*, 381 (IR diode, MW)
	Lander, D. R.; Unfried, K. G.; Stephens, J. W.; Glass, G. P.; Curl, R. F. *J. Phys. Chem.* 1989, *93*, 4109 (color and IR diode, reaction)	HBNH	Kawashima, Y.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* 1987, *87*, 6331 (IR diode)
(¹³CCH, C¹³CH)	Bogey, M.; Demuynck, C.; Destombes, J. L. *Mol. Phys.* 1989, *66*, 955 (submm wave)	C₃	Matsumura, K.; Kanamori, H.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* 1988, *89*, 3491 (IR diode, transient)
(CCD)	Yan, W.-B.; Warner, H. E.; Amano, T. *J. Chem. Phys.* 1991, *94*, 1712 (difference)		Kawaguchi, K.; Matsumura, K.; Kanamori, H.; Hirota, E. *J. Chem. Phys.* 1989, *91*, 1953 (IR diode)
HCCN	Saito, S.; Endo, Y.; Hirota, E. *J. Chem. Phys.* 1984, *80*, 1427 (MW)		Schmuttenmaer, C. A.; Cohen, R. C.; Pugliano, N.; Heath, J. R.; Cooksy, A. L.; Busarow, K. L.; Saykally, R. J. *Science* 1990, *249*, 897 (tunable FIR, ν₂)
	Brown, F. X.; Saito, S.; Yamamoto, S. *J. Mol. Spectrosc.* 1990, *143*, 203 (MW, dipole moment)		Sasada, H.; Amano, T.; Jarman, C.; Bernath, P. F. *J. Chem. Phys.* 1991, *94*, 2401 (near IR diode, b³Πg–a³Πu)
C₃H	Gottlieb, C. A.; Vrtilek, J. M.; Gottlieb, E. W.; Thaddeus, P.; Hjalmarson, Å. *Astrophys. J.* 1985, *294*, L55 (mm wave)	C₄	Heath, J. R.; Saykally, R. J. *J. Chem. Phys.* 1991, *94*, 3271 (IR diode, ν₃)
	Thaddeus, P.; Gottlieb, C. A.; Hjalmarson, Å.; Johansson, L. E. B.; Irvine, W. M.; Friberg, P.; Linke, R. A. *Astrophys. J.* 1985, *294*, L49 (radioastronomy)	C₅	Moazzen-Ahmadi, N.; McKellar, A. R. W.; Amano, T. *Chem. Phys. Lett.* 1989, *157*, 1 (IR diode)
	Gottlieb, C. A.; Gottlieb, E. W.; Thaddeus, P.; Vrtilek, J. M. *Astrophys. J.* 1986, *303*, 446 (MW)		Heath, J. R.; Cooksy, A. L.; Gruebele, M. H. W.; Schmuttenmaer, C. A.; Saykally, R. J. *Science* 1989, *244*, 564 (IR diode, ν₃)
			Moazzen-Ahmadi, N.; McKellar, A. R. W.; Amano, T. *J. Chem. Phys.* 1989, *91*, 2140 (IR diode, ν₃)

TABLE IV (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
C_7	Heath, J. R.; Saykally, R. J. *J. Chem. Phys.* **1991**, *94*, 1724 (IR diode, ν_4, $\nu_4 + \nu_7 - \nu_7$, $\nu_4 + 2\nu_7 - 2\nu_7$)	CCN	Fehér, M.; Salude, C.; Maier, J. P. *J. Mol. Spectrosc.* **1991**, *145*, 246 (IR diode, ν_1)
	Heath, J. R.; Van Orden, A.; Kuo, E.; Saykally, R. J. *Chem. Phys. Lett.* **1991**, *182*, 17 (IR diode, ν_5)	C_3N	Friberg, P.; Hjalmarson, A.; Irvine, W. M.; Guélin, M. *Astrophys. J.* **1980**, *241*, L99 (radioastronomy)
C_9	Heath, J. R.; Saykally, R. J. *J. Chem. Phys.* **1990**, *93*, 8392 (IR diode, ν_6)		Gottlieb, C. A.; Gottlieb, E. W.; Thaddeus, P.; Kawamura, H. *Astrophys. J.* **1983**, *275*, 916 (mm wave)
C_4Si	Ohishi, M.; Kaifu, N.; Kawaguchi, K.; Murakami, A.; Saito, S.; Yamamoto, S.; Ishikawa, S.; Fujita, Y.; Shiratori, Y.; Irvine, W. M. *Astrophys. J.* **1989**, *345*, L83 (radioastronomy)		Mikami, H.; Yamamoto, S.; Saito, S.; Guélin, M. *Astron. Astrophys.* **1989**, *217*, L5 (MW, excited vibrational states)
CCO	Yamada, C.; Saito, S.; Kanamori, H.; Hirota, E. *Astrophys. J.* **1985**, *290*, L65 (mm wave)	NCO	Carrington, A.; Fabris, A. R.; Lucas, N. J. D. *J. Chem. Phys.* **1968**, *49*, 5545 (EPR)
	Yamada, C.; Kanamori, H.; Horiguchi, H.; Tsuchiya, S.; Hirota, E. *J. Chem. Phys.* **1986**, *84*, 2573 (IR diode, transient)		Carrington, A.; Fabris, A. R.; Lucas, N. J. D. *Mol. Phys.* **1969**, *16*, 195 (EPR, excited vibrational states)
	Ohishi, M.; Suzuki, H.; Ishikawa, S.-I.; Yamada, C.; Kanamori, H.; Irvine, W. M.; Brown, R. D.; Godfrey, P. D.; Kaifu, N. *Astrophys. J.* **1991**, *380*, L39 (radioastronomy)		Saito, S.; Amano, T. *J. Mol. Spectrosc.* **1970**, *34*, 383 (MW)
CCS	Kaifu, N.; Suzuki, H.; Ohishi, M.; Miyaji, T.; Ishikawa, S.; Kasuga, T.; Morimoto, M.; Saito, S. *Astrophys. J.* **1987**, *317*, L111 (radioastronomy)		Carrington, A.; Fabris, A. R.; Howard, B. J.; Lucas, N. J. D. *Mol. Phys.* **1971**, *20*, 961 (EPR, excited vibrational states)
	Saito, S.; Kawaguchi, K.; Yamamoto, S.; Ohishi, M.; Suzuki, H.; Kaifu, N. *Astrophys. J.* **1987**, *317*, L115 (MW, radioastronomy)		Amano, T.; Hirota, E. *J. Chem. Phys.* **1972**, *57*, 5608 (MW, excited vibrational states)
	Yamamoto, S.; Saito, S.; Kawaguchi, K.; Chikada, Y.; Suzuki, H.; Kaifu, N.; Ishikawa, S.; Ohishi, M. *Astrophys. J.* **1990**, *361*, 318 (MW and radioastronomy)		Russell, D. K.; Beaudet, R. A. *Mol. Phys.* **1974**, *27*, 1645 (analysis of electronic spectra, hfs)
C_3O	Brown, R. D.; Godfrey, P. D.; Elmes, P. S.; Rodler, M.; Tack, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4112 (MW)		Barnes, C. E.; Brown, J. M.; Fackerell, A. D.; Sears, T. J. *J. Mol. Spectrosc.* **1982**, *92*, 485 (IR LMR)
	Tang, T. B.; Inokuchi, H.; Saito, S.; Yamada, C.; Hirota, E. *Chem. Phys. Lett.* **1985**, *116*, 83 (MW)		Kawaguchi, K.; Saito, S.; Hirota, E. *Mol. Phys.* **1983**, *49*, 663 (MW, excited vibrational states)
	Brown, R. D.; Godfrey, P. D.; Cragg, D. M.; Rice, E. H. N.; Irvine, W. M.; Friberg, P.; Suzuki, H.; Ohishi, M.; Kaifu, N.; Morimoto, M. *Astrophys. J.* **1985**, *297*, 302 (radioastronomy)		Kawaguchi, K.; Saito, S.; Hirota, E. *Mol. Phys.* **1985**, *55*, 341 (MW, excited vibrational states)
	Brown, R. D.; Pullin, D. E.; Rice, E. H. N.; Rodler, M. *J. Am. Chem. Soc.* **1985**, *107*, 7877 (IR, force field)		Werner, J.; Seebass, W.; Koch, M.; Curl, R. F.; Urban, W.; Brown, J. M. *Mol. Phys.* **1985**, *56*, 453 (IR LMR)
	McNaughton, D.; McGilvery, D.; Shanks, F. *J. Mol. Spectrosc.* **1991**, *149*, 458 (FTIR, ν_1)		Davies, P. B.; Davis, I. H. *Mol. Phys.* **1990**, *69*, 175 (FIR LMR)
C_3S	Yamamoto, S.; Saito, S.; Kawaguchi, K.; Kaifu, N.; Suzuki, H.; Ohishi, M. *Astrophys. J.* **1987**, *317*, L119 (MW, radioastronomy)	NCS	Carrington, A.; Fabris, A. R.; Lucas, N. J. D. *Mol. Phys.* **1969**, *16*, 195 (EPR)
			Amano, T.; Amano, Takako *J. Chem. Phys.* **1991**, *95*, 2275 (mm wave)
		N_3	Brazier, C. R.; Bernath, P. F.; Burkholder, J. B.; Howard, C. J. *J. Chem. Phys.* **1988**, *89*, 1762 (FTIR)
			Pahnke, R.; Ashworth, S. H.; Brown, J. M. *Chem. Phys. Lett.* **1988**, *147*, 179 (IR LMR)

^{a} For abbreviations for the method, see footnote a of Tables I–III. ^{b} See footnote b of Table II.

radical C_2H_5O. The methoxy radical is known to have a ^2E ground electronic state, and the ethoxy radical may be derived from methoxy by replacing one of the three hydrogen atoms of methoxy with a CH_3 group. The doubly degenerate state of methoxy is then split into two by this substitution of a methyl group, but the effect is not expected to be large, making the resulting two electronic states nearly degenerate. In fact, a preliminary calculation of Sung and Pitzer cited in ref 17 shows that the ground state is of A' symmetry and is 79 cm^{-1} lower in energy than the A'' state, although Miller et al. prefer the reverse ordering. Although the A rotational constant of ethoxy is much smaller than that of HCCO, its spin–rotation splittings are expected to be anomalous in view of this near degeneracy. When observed and analyzed in detail, they will provide detailed information on the low-lying electronic state.

B. Hyperfine Structure

When a free radical under consideration contains a nucleus with a finite spin, the nuclear spin interacts with other angular momenta, causing additional splittings in the spectra of the molecule, which are referred to as hyperfine structure. The interactions are classified

into three: those with the orbital angular momentum of the unpaired electron, those with the spin angular momentum of the unpaired electron, and the Fermi contact interaction. Frosch and Foley[18] have discussed the hyperfine interaction in a diatomic molecule and have shown that the splittings can be expressed by four main parameters, a, b, c, and d, which are defined as follows:

$$a = 2g_N\beta\beta_N\langle 1/r^3 \rangle \quad (7)$$

$$b = b_F - c/3 \quad (8)$$

$$b_F = (8\pi/3)g_S g_N\beta\beta_N|\psi(0)|^2 \quad (9)$$

$$c = (3/2)g_S g_N\beta\beta_N\langle(3\cos^2\theta - 1)/r^3\rangle \quad (10)$$

$$d = (3/2)g_S g_N\beta\beta_N\langle\sin^2\theta/r^3\rangle \quad (11)$$

In these equations, g_S and g_N denote the electron and nuclear g factors, respectively, β and β_N Bohr and nuclear magnetons, respectively, r and θ represent the location of the unpaired electron, expressed in a polar coordinate axis system with the z axis coinciding with the molecular axis and with the nucleus under consid-

TABLE V. Symmetric-Top Free Radicals[a]

species[b]	ref (method and comment)	species[b]	ref (method and comment)
SiH₃	Yamada, C.; Hirota, E. *Phys. Rev. Lett.* **1986**, *56*, 923 (IR diode, ν_2)		Hermann, H. W.; Leone, S. R. *J. Chem. Phys.* **1982**, *76*, 4766 (IR emission)
	Sugawara, K.; Nakanaga, T.; Takeo, H.; Matsumura, C. *Chem. Phys. Lett.* **1989**, *157*, 309 (IR diode, reaction)		Amano, T.; Bernath, P. F.; Yamada, C. *Nature* **1982**, *296*, 372 (difference, ν_3)
	Koda, S.; Suga, S.; Tsuchiya, S.; Suzuki, T.; Yamada, C.; Hirota, E. *Chem. Phys. Lett.* **1989**, *161*, 35 (IR diode, reaction)		Amano, T.; Bernath, P. F.; Yamada, C.; Endo, Y.; Hirota, E. *J. Chem. Phys.* **1982**, *77*, 5284 (difference, ν_3)
	Loh, S. K.; Beach, D. B.; Jasinski, J. M. *Chem. Phys. Lett.* **1990**, *169*, 55 (IR diode, reaction)		Hirota, E.; Yamada, C. *J. Mol. Spectrosc.* **1982**, *96*, 175 (IR diode and force field)
NO₃	Ishiwata, T.; Tanaka, I.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1985**, *82*, 2196 (IR diode, ν_3)		Yamada, C.; Hirota, E. *J. Chem. Phys.* **1983**, *78*, 669 (IR diode, ν_2 transition dipole)
	Friedl, R. R.; Sander, S. P. *J. Phys. Chem.* **1987**, *91*, 2721 (FTIR, ν_2 and ν_3)		Leone, S. R. *Acc. Chem. Res.* **1983**, *16*, 88 (IR emission)
	Kawaguchi, K.; Hirota, E.; Ishiwata, T.; Tanaka, I. *J. Chem. Phys.* **1990**, *93*, 951 (IR diode, ν_3)		Holt, P. L.; McCurdy, K. E.; Weisman, R. B.; Adams, J. S.; Engel, P. S. *J. Chem. Phys.* **1984**, *81*, 3349 (CARS, ν_1)
	Kawaguchi, K.; Ishiwata, T.; Tanaka, I.; Hirota, E. *Chem. Phys. Lett.* **1991**, *180*, 436 (FTIR)		Chu, J. O.; Flynn, G. W.; Chen, C. J.; Osgood, R. M., Jr. *Chem. Phys. Lett.* **1985**, *119*, 206 (IR emission)
CF₃	Endo, Y.; Yamada, C.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1982**, *77*, 3376 (MW)		Van Veen, G. N. A.; Baller, T.; De Vries, A. E. *Chem. Phys.* **1985**, *97*, 179 (TOF)
	Yamada, C.; Hirota, E. *J. Chem. Phys.* **1983**, *78*, 1703 (IR diode, ν_3)		Donaldson, D. J.; Leone, S. R. *J. Chem. Phys.* **1986**, *85*, 817 (IR emission)
	Brown, C. E.; Orlando, J. J.; Reid, J.; Smith, D. R. *Chem. Phys. Lett.* **1987**, *142*, 213; **1988**, *147*, 300 (IR diode, reaction)		Donaldson, D. J.; Leone, S. R. *J. Phys. Chem.* **1987**, *91*, 3128 (IR emission)
BH₃	Kawaguchi, K.; Butler, J. E.; Yamada, C.; Bauer, S. H.; Minowa, T.; Kanamori, H.; Hirota, E. *J. Chem. Phys.* **1987**, *87*, 2438 (IR diode, ν_2)		Continetti, R. E.; Balko, B. A.; Lee, Y. T. *J. Chem. Phys.* **1988**, *89*, 3383 (TOF)
			Kelly, P. B.; Westre, S. G. *Chem. Phys. Lett.* **1988**, *151*, 253 (resonance Raman)
CH₃S	Endo, Y.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1986**, *85*, 1770 (MW)	(CD₃)	Frye, J. M.; Sears, T. J.; Leitner, D. *J. Chem. Phys.* **1988**, *88*, 5300 (IR diode, ν_2)
CH₃O	Radford, H. E.; Russell, D. K. *J. Chem. Phys.* **1977**, *66*, 2222 (FIR LMR)	(CD₃)	Sears, T. J.; Frye, J. M.; Spirko, V.; Kraemer, W. P. *J. Chem. Phys.* **1989**, *90*, 2125 (IR diode, ν_2)
	Russell, D. K.; Radford, H. E. *J. Chem. Phys.* **1980**, *72*, 2750 (FIR LMR)		Wormhoudt, J.; McCurdy, K. E. *Chem. Phys. Lett.* **1989**, *156*, 47 (IR diode, ν_2 intensity)
	Endo, Y.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1984**, *81*, 122 (MW)	(CD₃)	Miller, J. T.; Burton, K. A.; Weismann, R. B.; Wu, W.-X.; Engel, P. S. *Chem. Phys. Lett.* **1989**, *158*, 179 (CARS, ν_1)
	Momose, T.; Endo, Y.; Hirota, E.; Shida, T. *J. Chem. Phys.* **1988**, *88*, 5338; **1989**, *90*, 4636 (submm wave)	(CD₃)	Westre, S. G.; Kelly, P. B. *J. Chem. Phys.* **1989**, *90*, 6977 (resonance Raman)
CH₃	Tan, L. Y.; Winer, A. M.; Pimentel, G. C. *J. Chem. Phys.* **1972**, *57*, 4028 (rapid-scan IR)	(CD₃)	Hall, G. E.; Sears, T. J.; Frye, J. M. *J. Chem. Phys.* **1989**, *90*, 6234 (IR diode, reaction)
	Yamada, C.; Hirota, E.; Kawaguchi, K. *J. Chem. Phys.* **1981**, *75*, 5256 (IR diode, ν_2)	(CD₃)	Fawzy, W. M.; Sears, T. J.; Davies, P. B. *J. Chem. Phys.* **1990**, *92*, 7021 (IR diode, ν_3)
	Laguna, G. A.; Baughcum, S. L. *Chem. Phys. Lett.* **1982**, *88*, 568 (IR diode, reaction)		Davies, P. B.; Martineau, P. M. *Appl. Phys. Lett.* **1990**, *57*, 237 (IR diode, CH_4 discharge plasma diagnosis)
	Baughcum, S. L.; Leone, S. R. *Chem. Phys. Lett.* **1982**, *89*, 183 (IR emission)		Sugawara, K.; Ito, F.; Nakanaga, T.; Takeo, H.; Matsumura, C. *J. Chem. Phys.* **1990**, *92*, 5328 (IR diode, reaction)
	Hermann, H. W.; Leone, S. R. *J. Chem. Phys.* **1982**, *76*, 4759 (IR emission)	(CD₃)	Hall, G. E.; Bout, D. V.; Sears, T. J. *J. Chem. Phys.* **1991**, *94*, 4182 (IR diode, reaction)

[a] For abbreviations for the method, see footnote a of Tables I–III.   [b] See footnote b of Table II.

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eration as the origin, and $\psi(0)$ stands for the value of the unpaired electron wavefunction at the nucleus. The treatment holds more or less for linear free radicals, although modifications may be required when the molecules are excited to bending states where they might lose axial symmetry. For the majority of non-linear free radicals, we may simply ignore the terms involving the orbital motion of the unpaired electron, because it is largely quenched. Exceptions include symmetric-top[19-24] and possibly spherical-top free radicals, for which the orbital angular momentum of the unpaired electron may not be completely quenched. The nuclear spin and unpaired electron spin dipolar interaction is represented by a tensor in a nonlinear molecule.

The hyperfine interactions which exist also in ordinary molecules add further complications to the spectra of free radicals. The most common among them is probably the nuclear electric quadrupole interaction, which almost all electrons in the molecule take part in.

As the definitions of the hyperfine coupling constants eqs 7–11 indicate, we may extract information on the distribution of the unpaired electron in the molecule from the observed coupling constants. The average of $1/r^3$ may be derived in two ways; one from the a constant and the other from the combination of c and d, or by taking the average of the angular part of c. However, it must be noted that the former corresponds to the average on the orbital motion of the electron, namely to the spatial average, whereas the latter reflects the distribution of the electron spin, which can thus be negative. This differentiation between the two averages is sometimes indicated by adding the suffix O or S to the average. The results on several diatomic free radicals show that the two averages agree closely with each other.

The spin averages may be compared with the values of free atoms;[25] the ratios give a rough idea about the spin density in the molecule. One might suspect that the Fermi term is closely related to the spin density as derived above. This actually holds for some nuclei, but fails for others. It is probably because the spin density reflects the distribution of the unpaired electron, whereas the Fermi term is affected also by the polari-
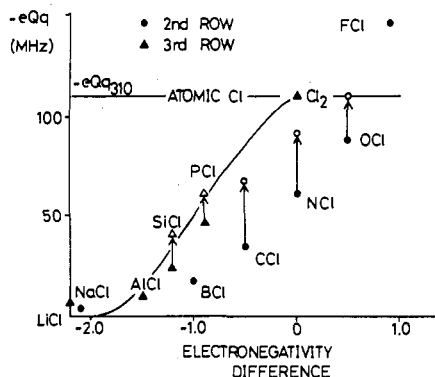
Figure 2. Chlorine nuclear quadrupole coupling constants of diatomic chlorides MCl plotted against the electronegativity difference, $x_M - x_{Cl}$. The solid curve represents a relation proposed by Gordy and Cook in ref 26 (reprinted from ref 27; copyright 1985 American Institute of Physics).

zation of inner core electron spins caused by the unpaired electron.

Gordy and Cook[26] proposed an S-shaped curve which correlates the nuclear quadrupole coupling constant of a diatomic molecule with the electronegativity difference of the component atoms, as shown by the solid curve in Figure 2. The nuclear quadrupole coupling constants obtained for free radicals, however, deviate from this curve considerably, if one uses the observed coupling constants without any corrections. Endo et al.[27] pointed out that for such diatomics we need to take into account back donation of π electrons. The extent of π electron back-donation may be estimated using the observed hyperfine coupling constants. Suppose that the spin density on the Cl atom in a molecule is ρ. If there are n π electrons in the highest occupied π orbital, the number of electrons in the highest and next-highest π orbitals localized on the Cl atom are approximately given by $n\rho$ and $4(1 - \rho)$, respectively, because the two orbitals are orthogonal with each other. The total number of p_π electrons transferred from Cl to the other atom, i.e. the number of back-donated π electrons is given by $4 - [n\rho + 4(1 - \rho)] = \rho(4 - n)$. The correction for back-donation is indicated by an arrow in Figure 2. It is obvious that this correction is essential for the Gordy and Cook relation to hold.

Very few hyperfine analyses have been reported for polyatomic free radicals, in particular for molecules which involve more than one nucleus with finite nuclear spin. Endo et al.[28,29] have investigated an interesting molecule, the vinoxy radical CH_2CHO, by microwave spectroscopy. They found that two of the three protons explained the main part of the hyperfine splittings, whereas the third one made only small contributions to the hyperfine structure of the four observed transitions. The observed dipolar coupling tensors of the two protons were examined in light of the molecular structure. This analysis led to the conclusion that the two protons are bonded to the terminal carbon atom, namely they are the methylene protons. Both the Fermi term and the dipolar coupling tensor components of these two protons correspond well to those in the related molecules, CH_2F[30] and CH_2Cl.[31] If we adopt McConnell's relation[32] and use the spin density of about 85% at the central carbon atoms in CH_2F and CH_2Cl as a reference, the spin density at the terminal carbon atom in vinoxy is estimated to be slightly less than 80%. Therefore, we may conclude that the ground state of

this molecule is better represented as formyl methyl $\cdot CH_2-CH{=}O$, rather than as ethenyloxy or vinoxy $CH_2{=}CH\text{-}O\cdot$. This conclusion is consistent with ab initio[33] and ESR[34] results.

III. Vibronic Interactions

As mentioned in the Introduction, most measurements with either microwave or infrared radiation are limited to the ground electronic state, and thus the effects of vibronic interactions do not appear conspicuously. However, thanks to the high resolution of these spectroscopic methods, the observed spectra often show some anomalous features which are best understood in terms of vibronic interactions. Here two types of molecules are discussed; one is the linear triatomic molecule and the other the symmetric-top molecule. In the former case, the vibration involved is either a parallel (σ) or a perpendicular (π) vibration, whereas in the latter the effect of a degenerate mode is discussed.

A. Linear Molecules

Johns[35,36] has found from the analysis of electronic spectra that two isoelectronic molecules BO_2 and CO_2^+ have unusually low $2\nu_3''$ frequencies: 2644 and 2938 cm^{-1}, respectively, which may be compared with the ν_3 frequency of CO_2 (2349 cm^{-1}). Kawaguchi et al.[37,38] measured the ν_3 fundamental frequencies of these two molecules using infrared diode laser spectroscopy to be 1278.2585 and 1423.0821 cm^{-1}, respectively. It should be noted that these fundamental frequencies are even smaller than half of the above-mentioned overtone frequencies derived from the electronic spectra, indicating that the vibrational anharmonicity is "negative" in the two molecules.

Kawaguchi et al.[37] have proposed a vibronic model to explain these anomalous features of the vibrational levels in the ground electronic state, namely they considered an off-diagonal term which has matrix elements between the $\tilde{X}^2\Pi_g$ ground state and the $\tilde{A}^2\Pi_u$ excited electronic state. Symmetry of the two electronic states requires the interaction term to be of σ_u symmetry, and this requirement is satisfied most simply if the term involves the antisymmetric stretching coordinate q_3 linearly, that is

$$H_{vibronic} = aq_3 \tag{12}$$

where a denotes the electronic matrix element between $\tilde{X}$ and $\tilde{A}$. We may then set up a two-dimensional matrix:

$$\begin{array}{c} \tilde{A}^2\Pi_u \\ \\ \tilde{X}^2\Pi_g \end{array} \begin{bmatrix} E + (1/2)fq_3^2 & aq_3 \\ \\ aq_3 & (1/2)fq_3^2 \end{bmatrix} \tag{13}$$

where the harmonic force constant f is assumed to be the same for the two electronic states for the sake of simplicity. This matrix may be solved using perturbation theory by treating q_3 as a parameter to derive an effective vibrational potential function for both the states:

$$V(\tilde{A}^2\Pi_u) =$$
$$E + (1/2)(f + 2a^2/E)q_3^2 - (a^4/E^3)q_3^4 + \dots \tag{14}$$

$$V(\tilde{X}^2\Pi_g) = (1/2)(f - 2a^2/E)q_3^2 + (a^4/E^3)q_3^4 + \dots \tag{15}$$

TABLE VI. Asymmetric-Top Free Radicals[a]

species[b]	ref (method and comment)	species[b]	ref (method and comment)
HO_2	Radford, H. E.; Evenson, K. M.; Howard, C. J. *J. Chem. Phys.* **1974**, *60*, 3178 (FIR LMR)		Bogey, M.; Davies, P. B.; Demuynck, C.; Destombes, J. L.; Sears, T. J. *Mol. Phys.* **1989**, *67*, 1033 (MW)
	Hougen, J. T.; Radford, H. E.; Evenson, K. M.; Howard, C. J. *J. Mol. Spectrosc.* **1975**, *56*, 210 (FIR LMR)		Bley, U.; Davies, P. B.; Grantz, M.; Sears, T. J.; Temps, F. *Chem. Phys.* **1991**, *152*, 281 (FIR LMR)
	Hougen, J. T. *J. Mol. Spectrosc.* **1975**, *54*, 447 (FIR LMR, analysis)	HSO (DSO)	Endo, Y.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1981**, *75*, 4379 (MW)
	Beers, Y.; Howard, C. J. *J. Chem. Phys.* **1975**, *63*, 4212 (MW)		Sears, T. J.; McKellar, A. R. W. *Mol. Phys.* **1983**, *49*, 25 (IR LMR, ν_3)
(DO$_2$)	Beers, Y.; Howard, C. J. *J. Chem. Phys.* **1976**, *64*, 1541 (MW)	FSO	Endo, Y.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1981**, *74*, 1568 (MW, hfs and dipole moment)
	Saito, S. *J. Mol. Spectrosc.* **1977**, *65*, 229 (MW)		Radford, H. E.; Wayne, F. D.; Brown, J. M. *J. Mol. Spectrosc.* **1983**, *99*, 209 (FIR LMR)
	Howard, C. J.; Evenson, K. M. *Geophys. Res. Lett.* **1977**, *4*, 437 (FIR LMR, reaction HO$_2$ + NO)	HS$_2$	Holstein, K. J.; Fink, E. H.; Wildt, J.; Zabel, F. *Chem. Phys. Lett.* **1985**, *113*, 1 (FTIR, Ã^{2}A' → X̃^{2}A'')
	Howard, C. J. *J. Chem. Phys.* **1977**, *67*, 5258 (FIR LMR, reaction HO$_2$ + NO$_2$)	HCO	Bowater, I. C.; Brown, J. M.; Carrington, A. *J. Chem. Phys.* **1971**, *54*, 4957 (EPR)
	Johns, J. W. C.; McKellar, A. R. W.; Riggin, M. *J. Chem. Phys.* **1978**, *68*, 3957 (IR LMR, ν_3)	(DCO)	Saito, S. *Astrophys. J.* **1972**, *178*, L95 (MW)
	Barnes, C. E.; Brown, J. M.; Carrington, A.; Pinkstone, J.; Sears, T. J.; Thistlethwaite, P. J. *J. Mol. Spectrosc.* **1978**, *72*, 86 (EPR)	(DCO)	Bolman, P. S. H.; Brown, J. M.; Carrington, A.; Lycett, G. J. *Proc. R. Soc. Lond.* **1973**, *A335*, 113 (EPR)
	Brown, J. M.; Sears, T. J. *J. Mol. Spectrosc.* **1979**, *75*, 111 (spin-rotation interaction, theory)		Austin, J. A.; Levy, D. H.; Gottlieb, C. A.; Radford, H. E. *J. Chem. Phys.* **1974**, *60*, 207 (MW)
(DO$_2$)	McKellar, A. R. W. *J. Chem. Phys.* **1979**, *71*, 81 (IR LMR, ν_2)		Cook, J. M.; Evenson, K. M.; Howard, C. J.; Curl, R. F., Jr. *J. Chem. Phys.* **1976**, *64*, 1381 (FIR LMR)
	Burrows, J. P.; Cliff, D. I.; Harris, G. W.; Thrush, B. A.; Wilkinson, J. P. T. *Proc. R. Soc. Lond.* **1979**, *A368*, 463 (FIR LMR, reaction)		Boland, B. J.; Brown, J. M.; Carrington, A. *Mol. Phys.* **1977**, *34*, 453 (EPR)
	Stimpfle, R. M.; Perry, R. A.; Howard, C. J. *J. Chem. Phys.* **1979**, *71*, 5183 (FIR LMR, reaction)		Brown, J. M.; Buttenshaw, J.; Carrington, A.; Parent, C. R. *Mol. Phys.* **1977**, *33*, 589 (IR LMR)
	Howard, C. J. *J. Chem. Phys.* **1979**, *71*, 2352 (FIR LMR, reaction)		Johns, J. W. C.; McKellar, A. R. W.; Riggin, M. *J. Chem. Phys.* **1977**, *67*, 2427 (IR LMR, ν_2)
	Saito, S.; Matsumura, C. *J. Mol. Spectrosc.* **1980**, *80*, 34 (MW, dipole moment)		Landsberg, B. M.; Merer, A. J.; Oka, T. *J. Mol. Spectrosc.* **1977**, *67*, 459 (laser Stark, ν_2)
	Brown, J. M.; Sears, T. J.; Watson, J. K. G. *Mol. Phys.* **1980**, *41*, 173 (spin-rotation interaction, theory)	(DCO)	Boland, B. J.; Brown, J. M.; Carrington, A.; Nelson, A. C. *Proc. R. Soc. Lond.* **1978**, *A360*, 507 (EPR)
	Howard, C. J.; Finlayson-Pitts, B. J. *J. Chem. Phys.* **1980**, *72*, 3842 (FIR LMR, reaction)		Brown, J. M.; Buttenshaw, J.; Carrington, A.; Dumper, K.; Parent, C. R. *J. Mol. Spectrosc.* **1980**, *79*, 47 (IR LMR)
	Zahniser, M. S.; Howard, C. J. *J. Chem. Phys.* **1980**, *73*, 1620 (FIR LMR, reaction)	(DCO)	Lowe, R. S.; McKellar, A. R. W. *J. Chem. Phys.* **1981**, *74*, 2686 (IR LMR, ν_1 and ν_3)
(DO$_2$)	Barnes, C. E.; Brown, J. M.; Radford, H. E. *J. Mol. Spectrosc.* **1980**, *84*, 179 (EPR, FIR LMR)		Brown, J. M.; Dumper, K.; Lowe, R. S. *J. Mol. Spectrosc.* **1983**, *97*, 441 (IR LMR, ν_2)
	Nagai, K.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1981**, *89*, 520 (IR diode, ν_2)		Blake, G. A.; Sastry, K. V. L. N.; De Lucia, F. C. *J. Chem. Phys.* **1984**, *80*, 95 (mm and submm wave)
	Charo, A.; De Lucia, F. C. *J. Mol. Spectrosc.* **1982**, *94*, 426 (mm and submm wave)	(DCO)	Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1988**, *127*, 540 (mm and submm wave)
(DO$_2$)	Uehara, H. *J. Chem. Phys.* **1982**, *77*, 3314 (IR LMR, ν_2 and ν_3)		Dane, C. B.; Lander, D. R.; Curl, R. F.; Tittel, F. K.; Guo, Y.; Ochsner, M. I. F.; Moore, C. B. *J. Chem. Phys.* **1988**, *88*, 2121 (color and IR diode, ν_1)
	Thrush, B. A.; Tyndall, G. S. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1469 (IR diode, reaction)		McKellar, A. R. W.; Burkholder, J. B.; Orlando, J. J.; Howard, C. J. *J. Mol. Spectrosc.* **1988**, *130*, 445 (FTIR, ν_3)
	Lee, Y.-P.; Howard, C. J. *J. Chem. Phys.* **1982**, *77*, 756 (FIR LMR, reaction)		Brown, J. M.; Radford, H. E.; Sears, T. J. *J. Mol. Spectrosc.* **1991**, *148*, 20 (FIR LMR, avoided crossing)
	Buchanan, J. W.; Thrush, B. A.; Tyndall, G. S. *Chem. Phys. Lett.* **1983**, *103*, 167 (IR diode, ν_3 intensity)	FCO	Nagai, K.; Yamada, C.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1981**, *90*, 249 (IR diode, ν_1 and ν_2)
(DO$_2$)	Saito, S.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1983**, *98*, 138 (MW)	CH$_2$	Mucha, J. A.; Evenson, K. M.; Jennings, D. A.; Ellison, G. B.; Howard, C. J. *Chem. Phys. Lett.* **1979**, *66*, 244 (FIR LMR)
	Yamada, C.; Endo, Y.; Hirota, E. *J. Chem. Phys.* **1983**, *78*, 4379 (difference, ν_1)		Sears, T. J.; Bunker, P. R.; McKellar, A. R. W. *J. Chem. Phys.* **1981**, *75*, 4731 (IR LMR, ν_2)
	Zahniser, M. S.; Stanton, A. C. *J. Chem. Phys.* **1984**, *80*, 4951 (IR diode, ν_3 intensity)		Sears, T. J.; Bunker, P. R.; McKellar, A. R. W.; Evenson, K. M.; Jennings, D. A.; Brown, J. M. *J. Chem. Phys.* **1982**, *77*, 5348 (FIR LMR, hfs)
(DO$_2$)	Lubic, K. G.; Amano, T.; Uehara, H.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1984**, *81*, 4826 (difference and IR diode, ν_1)		Sears, T. J.; Bunker, P. R.; McKellar, A. R. W. *J. Chem. Phys.* **1982**, *77*, 5363 (IR LMR, ν_2)
(DO$_2$)	Uehara, H.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1985**, *83*, 5479 (IR diode, ν_2 and ν_3)	(CD$_2$)	Bunker, P. R.; Sears, T. J.; McKellar, A. R. W.; Evenson, K. M.; Lovas, F. J. *J. Chem. Phys.* **1983**, *79*, 1211 (FIR LMR)
(DO$_2$)	Sears, T. J.; Takacs, G.; Howard, C. J.; Crownover, R. L.; Helminger, P.; De Lucia, F. C. *J. Mol. Spectrosc.* **1986**, *118*, 103 (FIR LMR, mm wave)	(CD$_2$)	McKellar, A. R. W.; Yamada, C.; Hirota, E. *J. Chem. Phys.* **1983**, *79*, 1220 (IR diode, ν_2)
FO$_2$	Yamada, C.; Hirota, E. *J. Chem. Phys.* **1984**, *80*, 4694 (IR diode, ν_2)		McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251 (FIR LMR, ã^{1}A$_1$)
	Kim, K. C.; Campbell, G. M. *Chem. Phys. Lett.* **1985**, *116*, 236 (IR diode, reaction)	(^{13}CH$_2$)	McKellar, A. R. W.; Sears, T. J. *Can. J. Phys.* **1983**, *61*, 480 (IR LMR, ν_2 and hfs)
	McKellar, A. R. W.; Burkholder, J. B.; Sinha, A.; Howard, C. J. *J. Mol. Spectrosc.* **1987**, *125*, 288 (FTIR)		

TABLE VI (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
	Petek, H.; Nesbitt, D. J.; Ogilby, P. R.; Moore, C. B. *J. Phys. Chem.* 1983, 87, 5367 (difference, ν_1 and ν_3)		Seaquist, E. R.; Bell, M. B. *Astrophys. J.* 1986, 303, L67 (radioastronomy)
(CD$_2$)	Evenson, K. M.; Sears, T. J.; McKellar, A. R. W. *J. Opt. Soc. Am.* 1984, B1, 15 (FIR LMR, excited vibrational states)	(^{13}CC$_2$H$_2$)	Bogey, M.; Destombes, J. L. *Astron. Astrophys.* 1986, 159, L8 (mm wave)
	Sears, T. J.; McKellar, A. R. W.; Bunker, P. R.; Evenson, K. M.; Brown, J. M. *Astrophys. J.* 1984, 276, 399 (IR and FIR LMR)	(^{13}CC$_2$H$_2$)	Gómez-González, J.; Guélin, M.; Cernicharo, J.; Kahane, C.; Bogey, M. *Astron. Astrophys.* 1986, 168, L11 (radioastronomy)
	Sears, T. J. *J. Chem. Phys.* 1986, 85, 3711 (IR diode)		Bogey, M.; Demuynck, C.; Destombes, J. L. *Chem. Phys. Lett.* 1986, 125, 383 (MW)
	Marshall, M. D.; McKellar, A. R. W. *J. Chem. Phys.* 1986, 85, 3716 (IR diode, ν_2)	(^{13}CC$_2$H$_2$)	Madden, S. C.; Irvine, W. H.; Matthews, H. E. *Astrophys. J.* 1986, 311, L27 (radioastronomy)
	Petek, H.; Nesbitt, D. J.; Darwin, D. C.; Ogilby, P. R.; Moore, C. B.; Ramsay, D. A. *J. Chem. Phys.* 1989, 91, 6566 (difference, ã^{1}A$_1$ ν_1/ν_3)	(C$_3$HD)	Bell, M. B.; Feldman, P. A.; Matthews, H. E.; Avery, L. W. *Astrophys. J.* 1986, 311, L89 (radioastronomy)
CF$_2$	Powell, F. X.; Lide, D. R., Jr. *J. Chem. Phys.* 1966, 45, 1067 (MW)		Matthews, H. E.; Madden, S. C.; Avery, L. W.; Irvine, W. M. *Astrophys. J.* 1986, 307, L69 (radioastronomy)
	Kirchhoff, W. H.; Lide, D. R., Jr.; Powell, F. X. *J. Mol. Spectrosc.* 1973, 47, 491 (MW, force field and dipole moment)		Bogey, M.; Demuynck, C.; Destombes, J. L.; Dubus, H. *J. Mol. Spectrosc.* 1987, 122, 313 (mm wave)
	Davies, P. B.; Lewis-Bevan, W.; Russell, D. K. *J. Chem. Phys.* 1981, 75, 5602 (IR diode, ν_1)	(deuterated species)	Gerin, M.; Wooteen, H. A.; Combes, F.; Boulanger, F.; Peters III, W. L.; Kuiper, T. B. H.; Encrenaz, P. J.; Bogey, M. *Astron. Astrophys.* 1987, 173, L1 (radioastronomy)
	Charo, A.; De Lucia, F. C. *J. Mol. Spectrosc.* 1982, 94, 363 (mm and submm wave)		Kanata, H.; Yamamoto, S.; Saito, S. *Chem. Phys. Lett.* 1987, 140, 221 (MW, dipole moment)
	Davies, P. B.; Hamilton, P. A.; Elliott, J. M.; Rice, M. J. *J. Mol. Spectrosc.* 1983, 102, 193 (IR diode, ν_3)	(C$_3$HD)	Bell, M. B.; Watson, J. K. G.; Feldman, P. A.; Matthews, H. E.; Madden, S. C.; Irvine, W. M. *Chem. Phys. Lett.* 1987, 136, 588 (radioastronomy, hfs)
	Sugawara, K.; Nakanaga, T.; Takeo, H.; Matsumura, C. *Chem. Phys. Lett.* 1986, 130, 560 (IR diode, reaction)		Vrtílek, J. M.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J.* 1987, 314, 716 (MW, radioastronomy)
	Sugawara, K.; Nakanaga, T.; Takeo, H.; Matsumura, C. *Chem. Phys. Lett.* 1987, 134, 347 (IR diode, reaction)		Hirahara, Y.; Masuda, A.; Kawaguchi, K. *J. Chem. Phys.* 1991, 95, 3975 (FTIR, ν_3)
	Orlando, J. J.; Reid, J.; Smith, D. R. *Chem. Phys. Lett.* 1987, 141, 423; 1988, 147, 300 (IR diode, reaction)	SiH$_2$	Yamada, C.; Kanamori, H.; Hirota, E.; Nishiwaki, N.; Itabashi, N.; Kato, K.; Goto, T. *J. Chem. Phys.* 1989, 91, 4582 (IR diode, ν_2)
	Burkholder, J. B.; Howard, C. J.; Hamilton, P. A. *J. Mol. Spectrosc.* 1988, 127, 362 (FTIR, ν_1 and ν_3)	SiF$_2$	Rao, V. M.; Curl, R. F., Jr.; Timms, P. L.; Margrave, J. L. *J. Chem. Phys.* 1965, 43, 2557 (MW)
	Wormhoudt, J.; McCurdy, K. E.; Burkholder, J. B. *Chem. Phys. Lett.* 1989, 158, 480 (FTIR)		Rao, V. M.; Curl, R. F., Jr. *J. Chem. Phys.* 1966, 45, 2032 (MW)
	Suto, O.; Steinfeld, J. *Chem. Phys. Lett.* 1990, 168, 181 (IR diode, reaction)		Khanna, V. M.; Hauge, R.; Curl, R. F., Jr.; Margrave, J. L. *J. Chem. Phys.* 1967, 47, 301 (IR)
CCl$_2$	Fujitake, M.; Hirota, E. *J. Chem. Phys.* 1989, 91, 3426 (mm and submm wave)		Shoji, H.; Tanaka, T.; Hirota, E. *J. Mol. Spectrosc.* 1973, 47, 268 (MW, ν_1/ν_3 Coriolis)
HNO (DNO)	Takagi, K.; Saito, S. *J. Mol. Spectrosc.* 1972, 44, 81 (MW)		Caldow, G. L.; Deeley, C. M.; Turner, P. H.; Mills, I. M. *Chem. Phys. Lett.* 1981, 82, 434 (FTIR, ν_1 and ν_3)
	Saito, S.; Takagi, K. *Astrophys. J.* 1972, 175, L47 (MW)	SiCl$_2$	Tanimoto, M.; Takeo, H.; Matsumura, C.; Fujitake, M.; Hirota, E. *J. Chem. Phys.* 1989, 91, 2102 (MW)
	Saito, S.; Takagi, K. *J. Mol. Spectrosc.* 1973, 47, 99 (MW)	C$_2$Si	Thaddeus, P.; Cummins, S. E.; Linke, R. A. *Astrophys. J.* 1984, 283, L45 (radioastronomy)
(DNO)	Johns, J. W. C.; McKellar, A. R. W. *J. Chem. Phys.* 1977, 66, 1217 (laser Stark, ν_2 and ν_3 for HNO and ν_1 and ν_2 for DNO)		Snyder, L. E.; Henkel, C.; Hollis, J. M.; Lovas, F. J. *Astrophys. J.* 1985, 290, L29 (radioastronomy)
	Takagi, K.; Saito, S.; Kakimoto, M.; Hirota, E. *J. Chem. Phys.* 1980, 73, 2570 (MODR, Ã^{1}A''(100))		Suenram, R. D.; Lovas, F. J.; Matsumura, K. *Astrophys. J.* 1989, 342, L103 (MW, dipole moment)
(DNO)	Johns, J. W. C.; McKellar, A. R. W.; Weinberger, E. *Can. J. Phys.* 1983, 61, 1106 (FTIR, ν_1)		Gottlieb, C. A.; Vrtílek, J. M.; Thaddeus, P. *Astrophys. J.* 1989, 343, L29 (mm wave)
(DNO)	Sastry, K. V. L. N.; Helminger, P.; Plummer, G. M.; Herbst, E.; De Lucia, F. C. *Astrophys. J. Suppl.* 1984, 55, 563 (mm and submm wave)	(Si^{13}CC)	Cernicharo, J.; Guélin, M.; Kahane, C.; Bogey, M.; Demuynck, C.; Destombes, J. L. *Astron. Astrophys.* 1991, 246, 213 (MW, radioastronomy)
(DNO)	Petersen, J. C.; Amano, T.; Ramsay, D. A. *J. Chem. Phys.* 1984, 81, 5449 (MODR, Ã^{1}A''(000))	Si$_2$H$_2$	Bogey, M.; Bolvin, H.; Demuynck, C.; Destombes, J. L. *Phys. Rev. Lett.* 1991, 66, 413 (submm wave, nonclassical form)
	Petersen, J. C.; Saito, S.; Amano, T.; Ramsay, D. A. *Can. J. Phys.* 1984, 62, 1731 (MODR, Ã^{1}A''(000))	GeF$_2$	Hastie, J. W.; Hauge, R.; Margrave, J. L. *J. Phys. Chem.* 1968, 72, 4492 (IR)
	Takagi, K.; Suzuki, T.; Saito, S.; Hirota, E. *J. Chem. Phys.* 1985, 83, 535 (MODR, dipole moment in Ã^{1}A''(100))		Takeo, H.; Curl, R. F., Jr.; Wilson, P. W. *J. Mol. Spectrosc.* 1971, 38, 464 (MW)
	Takagi, K.; Saito, S.; Suzuki, T.; Hirota, E. *J. Chem. Phys.* 1986, 84, 1317 (MODR, Ã^{1}A''(020))		Takeo, H.; Curl, R. F., Jr. *J. Mol. Spectrosc.* 1972, 43, 21 (MW)
HPO	Saito, S.; Endo, Y.; Hirota, E. *J. Chem. Phys.* 1986, 84, 1157 (MW)	NH$_2$	Davies, P. B.; Russell, D. K.; Thrush, B. A.; Wayne, F. D. *J. Chem. Phys.* 1975, 62, 3739 (FIR LMR)
C$_3$H$_2$	Thaddeus, P.; Guélin, M.; Linke, R. A. *Astrophys. J.* 1981, 246, L41 (radioastronomy)		Hills, G. W.; Cook, J. M.; Curl, R. F., Jr.; Tittel, F. K. *J. Chem. Phys.* 1976, 65, 823 (MODR, hfs)
	Matthews, H. E.; Irvine, W. H. *Astrophys. J.* 1985, 298, L61 (radioastronomy)		Hills, G. W.; Cook, J. M. *Astrophys. J.* 1976, 209, L157 (MW)
	Thaddeus, P.; Vrtílek, J. M.; Gottlieb, C. A. *Astrophys. J.* 1985, 299, L63 (mm wave, radioastronomy)		

TABLE VI (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
	Davies, P. B.; Russell, D. K.; Thrush, B. A.; Radford, H. E. *Chem. Phys. Lett.* **1976**, *42*, 35 (FIR LMR, hfs)		Brown, R. D.; Burden, F. R.; Godfrey, P. D.; Gillard, I. R. *J. Mol. Spectrosc.* **1974**, *52*, 301 (MW)
	Cook, J. M.; Hills, G. W.; Curl, R. F., Jr. *Astrophys. J.* **1976**, *207*, L139 (MODR)		Davies, P. B.; Handy, B. J.; Russell, D. K. *Chem. Phys. Lett.* **1979**, *68*, 395 (IR diode, ν_1 and ν_3)
	Cook, J. M.; Hills, G. W.; Curl, R. F., Jr. *J. Chem. Phys.* **1977**, *67*, 1450 (MODR)		Hakuta, K.; Uehara, H. *J. Chem. Phys.* **1981**, *74*, 5995 (IR LMR, ν_1)
	Hills, G. W.; Curl, R. F., Jr. *J. Chem. Phys.* **1977**, *66*, 1507 (MODR, Ã^{2}A$_1$)		Davies, P. B.; Kho, C. J.; Leong, W. K.; Lewis-Bevan, W. *J. Chem. Soc., Chem. Commun.* **1982**, 690 (IR diode, reaction)
	Davies, P. B.; Russell, D. K.; Thrush, B. A.; Radford, H. E. *Proc. R. Soc. Lond.* **1977**, *A353*, 299 (FIR LMR)		Davies, P. B.; Hamilton, P. A.; Lewis-Bevan, W.; Russell, D. K. *Proc. R. Soc. Lond.* **1984**, *A392*, 445 (IR diode, ν_1)
	Brown, J. M.; Buttenshaw, J.; Carrington, A.; Parent, C. R. *Mol. Phys.* **1977**, *33*, 589 (IR LMR, ν_2)		Davies, P. B.; Hamilton, P. A. *Proc. R. Soc. Lond.* **1984**, *A393*, 397 (IR diode, ν_3)
	Hills, G. W.; Lowe, R. S.; Cook, J. M.; Curl, R. F., Jr. *J. Chem. Phys.* **1978**, *68*, 4073 (MODR)		Uehara, H.; Horiai, K. *J. Chem. Phys.* **1986**, *84*, 5568 (IR LMR, ν_3)
	Lowe, R. S.; Kasper, J. V. V.; Hills, G. W.; Dillenschneider, W.; Curl, R. F., Jr. *J. Chem. Phys.* **1979**, *70*, 3356 (MODR, Ã^{2}A$_1$)		Frank, V. E.; Hüttner, W. *Chem. Phys.* **1991**, *152*, 261 (MW, Zeeman)
	Hills, G. W.; McKellar, A. R. W. *J. Mol. Spectrosc.* **1979**, *74*, 224 (IR LMR, ν_2)	PH$_2$	Davies, P. B.; Russell, D. K.; Thrush, B. A. *Chem. Phys. Lett.* **1976**, *37*, 43 (FIR LMR)
(ND$_2$)	Hills, G. W.; McKellar, A. R. W. *J. Chem. Phys.* **1979**, *71*, 3330 (IR LMR, ν_2)		Hills, G. W.; McKellar, A. R. W. *J. Chem. Phys.* **1979**, *71*, 1141 (IR LMR, ν_2)
	Brown, J. M.; Sears, T. J. *J. Mol. Spectrosc.* **1979**, *75*, 111 (spin–rotation, theory)		Davies, P. B.; Russell, D. K.; Thrush, B. A.; Radford, H. E. *Chem. Phys. Lett.* **1979**, *44*, 421 (FIR LMR)
	Brown, J. M.; Sears, T. J.; Watson, J. K. G. *Mol. Phys.* **1980**, *41*, 173 (spin–rotation, theory)		Birss, F. W.; Lessard, G.; Thrush, B. A.; Ramsay, D. A. *J. Mol. Spectrosc.* **1982**, *92*, 269 (molecular constants)
	Kawaguchi, K.; Yamada, C.; Hirota, E.; Brown, J. M.; Buttenshaw, J.; Parent, C. R.; Sears, T. J. *J. Mol. Spectrosc.* **1980**, *81*, 60 (IR LMR, ν_2)		Endo, Y.; Saito, S.; Hirota, E. *J. Mol. Spectrosc.* **1983**, *97*, 204 (MW)
(NHD)	Steimle, T. C.; Brown, J. M.; Curl, R. F., Jr. *J. Chem. Phys.* **1980**, *73*, 2552 (MODR)		Kajita, M.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1987**, *124*, 66 (MW)
	Charo, A.; Sastry, K. V. L. N.; Herbst, E.; De Lucia, F. C. *Astrophys. J.* **1981**, *244*, L111 (mm and submm wave)	PF$_2$	Saito, S.; Endo, Y.; Hirota, E. *J. Chem. Phys.* **1986**, *85*, 1778 (MW)
	Vervloet, M.; Merienne-Lafore, M. F. *Can. J. Phys.* **1982**, *60*, 49 (IR emission, ν_1 and ν_3)	PO$_2$	Kawaguchi, K.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1985**, *82*, 4893 (FIR LMR, MW)
	Amano, T.; Bernath, P. F.; McKellar, A. R. W. *J. Mol. Spectrosc.* **1982**, *94*, 100 (difference, ν_1 and ν_3)	CH$_2$F	Mucha, J. A.; Jennings, D. A.; Evenson, K. M.; Hougen, J. T. *J. Mol. Spectrosc.* **1977**, *68*, 122 (FIR LMR)
	Hills, G. W.; Cook, J. M. *J. Mol. Spectrosc.* **1982**, *94*, 456 (MODR, fs and hfs)		Endo, Y.; Yamada, C.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1983**, *79*, 1605 (MW)
	Hills, G. W.; Brazier, C. R.; Brown, J. M.; Cook, J. M.; Curl, R. F., Jr. *J. Chem. Phys.* **1982**, *76*, 240 (MODR, Ã^{2}A$_1$)		Yamada, C.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *116*, 101 (IR diode, ν_3)
(NHD)	Carrington, A.; Geiger, J. S.; Smith, D. R.; Bonnett, J. D.; Brown, C. *Chem. Phys. Lett.* **1982**, *90*, 6 (FIR LMR)	CH$_2$Cl	Endo, Y.; Saito, S.; Hirota, E. *Can. J. Phys.* **1984**, *62*, 1347 (MW)
	Amano, T.; Kawaguchi, K.; Kakimoto, M.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1982**, *77*, 159 (IR–optical double resonance)	CH$_2$OH	Radford, H. E.; Evenson, K. M.; Jennings, D. A. *Chem. Phys. Lett.* **1981**, *78*, 589 (FIR LMR)
	Merienne-Lafore, M.-F.; Vervloet, M. *J. Mol. Spectrosc.* **1984**, *108*, 160 (emission, $3\nu_2$)	CH$_2$CN	Irvine, W. M.; Friberg, P.; Hjalmarson, Å.; Ishikawa, S.; Kaifu, N.; Kawaguchi, K.; Madden, S. C.; Matthews, H. E.; Ohishi, M.; Saito, S.; Suzuki, H.; Thaddeus, P.; Turner, B. E.; Yamamoto, S.; Ziurys, L. M. *Astrophys. J.* **1988**, *334*, L107 (radioastronomy)
(ND$_2$)	Muenchausen, R. E.; Hills, G. W.; Merienne-Lafore, M. F.; Ramsay, D. A.; Vervloet, M.; Birss, F. W. *J. Mol. Spectrosc.* **1985**, *112*, 203 (molecular constants)		Saito, S.; Yamamoto, S.; Irvine, W. M.; Ziurys, L. M.; Suzuki, H.; Ohishi, M.; Kaifu, N. *Astrophys. J.* **1988**, *334*, L113 (MW)
(ND$_2$)	Chichinin, A. I.; Krasnoperov, L. N. *Chem. Phys. Lett.* **1985**, *115*, 343 (IR LMR, vibrational relaxation)		Turner, B. E.; Friberg, P.; Irvine, W. M.; Saito, S.; Yamamoto, S. *Astrophys. J.* **1990**, *355*, 546 (radioastronomy)
	Kawaguchi, K.; Suzuki, T.; Saito, S.; Hirota, E. *J. Opt. Soc. Am.* **1987**, *B4*, 1203 (IR–optical double resonance)	H$_2$CCC	Vrtilek, J. M.; Gottlieb, C. A.; Gottlieb, E. W.; Killian, T. C.; Thaddeus, P. *Astrophys. J.* **1990**, *364*, L53 (mm wave)
	Burkholder, J. B.; Howard, C. J.; McKellar, A. R. W. *J. Mol. Spectrosc.* **1988**, *127*, 415 (FTIR, ν_2)		Cernicharo, J.; Gottlieb, C. A.; Guélin, M.; Killian, T. C.; Paubert, G.; Thaddeus, P.; Vrtilek, J. M. *Astrophys. J.* **1991**, *368*, L39 (radioastronomy)
	Curl, R. F.; Murray, K. K.; Petri, M.; Richnow, M. L.; Tittel, F. K. *Chem. Phys. Lett.* **1989**, *161*, 98 (color, jet)	H$_2$CCCC	Killian, T. C.; Vrtilek, J. M.; Gottlieb, C. A.; Gottlieb, E. W.; Thaddeus, P. *Astrophys. J.* **1990**, *365*, L89 (mm wave)
	Cohen, R. C.; Busarow, K. L.; Schmuttenmaer, C. A.; Lee, Y. T.; Saykally, R. J. *Chem. Phys. Lett.* **1989**, *164*, 321 (tunable FIR)		Cernicharo, J.; Gottlieb, C. A.; Guélin, M.; Killian, T. C.; Thaddeus, P.; Vrtilek, J. M. *Astrophys. J.* **1991**, *368*, L43 (radioastronomy)
	McKellar, A. R. W.; Vervloet, M.; Burkholder, J. B.; Howard, C. J. *J. Mol. Spectrosc.* **1990**, *142*, 319 (FTIR, emission, ν_1, ν_3, and $2\nu_2$)	NH$_2$O	Davies, P. B.; Dransfeld, P.; Temps, F.; Wagner, H. Gg. *J. Chem. Phys.* **1984**, *81*, 3763 (FIR LMR)
(ND$_2$)	Kanada, M.; Yamamoto, S.; Saito, S. *J. Chem. Phys.* **1991**, *94*, 3423 (MW)		Mikami, H.; Saito, S.; Yamamoto, S. *J. Chem. Phys.* **1991**, *94*, 3415 (MW)
NF$_2$	Hrubesh, L. W.; Rinehart, E. A.; Anderson, R. E. *J. Mol. Spectrosc.* **1970**, *36*, 354 (MW)	HCCO	Endo, Y.; Hirota, E. *J. Chem. Phys.* **1987**, *86*, 4319 (submm wave)

TABLE VI (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
	Unfried, K. G.; Glass, G. P.; Curl, R. F. *Chem. Phys. Lett.* **1991**, *177*, 33 (IR diode, ν_2, reaction)		Deroche, J.-C.; Bürger, H.; Schulz, P.; Willner, H. *J. Mol. Spectrosc.* **1981**, *89*, 269 (IR)
C_2H_3	Kanamori, H.; Endo, Y.; Hirota, E. *J. Chem. Phys.* **1990**, *92*, 197 (IR diode, CH_2 wagging band)	SSO	Meschi, D. J.; Myers, R. J. *J. Mol. Spectrosc.* **1959**, *3*, 405 (MW, dipole moment)
C_2H_3O	Endo, Y.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1985**, *83*, 2026 (MW)		Cook, R. L.; Winnewisser, G.; Lindsey, D. C. *J. Mol. Spectrosc.* **1973**, *46*, 276 (MW)
	Endo, Y.; Tsuchiya, S.; Yamada, C.; Hirota, E.; Koda, S. *J. Chem. Phys.* **1986**, *85*, 4446 (MW, reaction)		Tiemann, E.; Hoeft, J.; Lovas, F. J.; Johnson, D. R. *J. Chem. Phys.* **1974**, *60*, 5000 (MW)
(C_2D_3O)	Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1988**, *127*, 535 (submm wave)		Lindenmayer, J.; Jones, H. *J. Mol. Spectrosc.* **1985**, *112*, 71 (IR diode, ν_1)
cyclic-C_3H	Yamamoto, S.; Saito, S.; Ohishi, M.; Suzuki, H.; Ishikawa, S.; Kaifu, N.; Murakami, A. *Astrophys. J.* **1987**, *322*, L55 (MW, radioastronomy)	$(SS^{18}O)$	Lindenmayer, J. *J. Mol. Spectrosc.* **1986**, *116*, 315 (MW)
(C_3D)	Yamamoto, S.; Saito, S. *Astrophys. J.* **1990**, *363*, L13 (MW)	$(SS^{18}O)$	Lindenmayer, J.; Dieter Rudolph, H.; Jones, H. *J. Mol. Spectrosc.* **1986**, *119*, 56 (IR diode, ν_1 and ν_3 for $S_2^{18}O$ and ν_3 for $S_2^{16}O$)
SF_2	Johnson, D. R.; Powell, F. X. *Science* **1969**, *164*, 950 (MW)	S_2O_2(cis)	Lovas, F. J.; Tiemann, E.; Johnson, D. R. *J. Chem. Phys.* **1974**, *60*, 5005 (MW)
	Kirchhoff, W. H.; Johnson, D. R.; Powell, F. X. *J. Mol. Spectrosc.* **1973**, *48*, 157 (MW)	ClOOCl	Birk, M.; Friedl, R. R.; Cohen, E. A.; Pickett, H. M.; Sander, S. P. *J. Chem. Phys.* **1989**, *91*, 6588 (MW)
	Endo, Y.; Saito, S.; Hirota, E.; Chikaraishi, T. *J. Mol. Spectrosc.* **1979**, *77*, 222 (MW)		Burkholder, J. B.; Orlando, J. J.; Howard, C. J. *J. Phys. Chem.* **1990**, *94*, 687 (FTIR)

[a] For abbreviations for the method, see footnote *a* of Tables I–III. [b] See footnote *b* of Table II.

Kawaguchi et al. applied small corrections for the vibrational anharmonicity constants x_{13}, x_{23}, and x_{33} to the observed frequencies of ν_3 and $2\nu_3$. The corrected frequencies are 1317.71 and 2747.40 cm^{-1} for $^{11}BO_2$ and 1479.2 and 3057.2 cm^{-1} for CO_2^+. The electronic energy of the $\tilde{A}$ state E is calculated from the band origin of the $\tilde{A}$–$\tilde{X}$ transition corrected for zero-point energy: 17651 and 27600 cm^{-1} for BO_2 and CO_2^+, respectively. The two vibrational frequencies then yield the effective harmonic force constant $f - 2a^2/E$ and the interaction constant a to be 3.37 mdyn/Å, 0.000993 dyn for BO_2 and 4.56 mdyn/Å, 0.00154 dyn for CO_2^+. In order to check this model, Kawaguchi et al. calculated the $2\nu_3$ frequency in the $\tilde{A}$ state. The calculated values after being corrected for the anharmonicity are 4714 and 5462 cm^{-1} for the two molecules, respectively, which compare favorably with the observed values, 4702 and 5572 cm^{-1}, respectively.[35,36]

Another example of a linear molecule is the CCH radical. Kanamori and Hirota[39] detected a vibrational state of Π symmetry at 2166.21280 cm^{-1}, which is fairly close to another Π state $\nu_2 + \nu_3$ at 2090.82066 cm^{-1}.[40] Because the ν_2 frequency is 371.60337 cm^{-1}, they concluded that the Π band should be assigned to either $7\nu_2$ or $5\nu_3$, the former being slightly more reasonable. Ervin and Lineberger[41] have recently carried out a photodetachment experiment of CCH$^-$ and observed three vibrational states of the CCH neutral at 365, 790, and 1240 cm^{-1} within the $\tilde{X}^2\Sigma^+$ ground electronic manifold, which they assigned to ν_2, $2\nu_2$, and $3\nu_2$, respectively. An extrapolation of these levels confirmed that the state Kanamori and Hirota detected was in fact $5\nu_2$, rather than $7\nu_2$. This result means that the vibrational anharmonicity associated with the ν_2 mode of CCH is "negative".

The lowest excited electronic state of CCH is known to be a Π state. Although its location has not been determined precisely, spectroscopic[42] and ab initio[43] results have indicated that it is very likely to be around 3600 cm^{-1}. Because this is a Π state, it is coupled with the ground Σ state through the bending mode. The vibronic interaction Hamiltonian may be of the form

$$H_{vibronic} = V_1 q\{\exp[i(\theta - \alpha)] + \exp[-i(\theta - \alpha)]\} + \dots \quad (16)$$

where $q_\pm = q\ \exp[\pm i\alpha]$ denote the degenerate bending coordinates and θ stands for the azimuthal angle of the unpaired electron. When the matrix element of the electronic operator V_1 is designated by h_1, we have again a two-dimensional matrix, where the vibrational coordinates are treated as parameters:

$$\begin{array}{c} \tilde{A}^2\Pi \\ \tilde{X}^2\Sigma^+ \end{array} \begin{bmatrix} E + (1/2)\omega q^2 + \dots & h_1 q_+ \\ h_1^* q_- & (1/2)\omega q^2 + \dots \end{bmatrix} \quad (17)$$

An approximate solution for the ground state is then given by

$$V_{eff}(\tilde{X}) = (1/2)\omega q^2 - [|h_1|^2/E]q^2 + [|h_1|^4/E^3]q^4 + \dots \quad (18)$$

Kawaguchi et al.[40] have employed a similar model to explain the small spin–orbit coupling constants that were needed to reproduce spectra observed for vibronic Π levels in the ground electronic Σ state. They thus estimated $|h_1|$ to be about 680 cm^{-1}, provided that E was about 3700 cm^{-1}. When these values are transferred to V_{eff}, the harmonic frequency is reduced by $2|h_1|^2/E = 250$ cm^{-1} and the vibrational anharmonicity is given by $\omega x = (3/2)|h_1|^4/E^3 = 6.3$ cm^{-1}. The latter value may be compared with 15.8 cm^{-1} as required to reproduce the data of Ervin and Lineberger.[41]

B. Symmetric-Top Molecules

The discussion on the Σ–Π interaction in a linear molecule may be extended to the case of a symmetric-top molecule, where the vibrational mode involved is doubly degenerate.[44] One state is assumed to be nondegenerate (of A symmetry), whereas the other is doubly degenerate (of E symmetry). The latter is taken to be higher in energy than the former by E.

TABLE VII. Ionic Species[a]

species[b]	ref (method and comment)	species[b]	ref (method and comment)
atomic ions		diatomic ions	
N[+]	Cooksy, A. L.; Hovde, D. C.; Saykally, R. J. *J. Chem. Phys.* **1986**, *84*, 6101; **1988**, *89*, 5968 (FIR LMR)	(diamagnetic species)	
Ne[+]	Yamada, C.; Kanamori, H.; Hirota, E. *J. Chem. Phys.* **1985**, *83*, 552 (IR diode)	CH[+]	Carrington, A.; Buttenshaw, J.; Kennedy, R. A.; Softley, T. P. *Mol. Phys.* **1982**, *45*, 747 (CO$_2$ laser, Doppler tuning)
Ar^{+}	Davies, P. B.; Hamilton, P. A. *Chem. Phys. Lett.* **1983**, *94*, 565 (IR diode)		Carrington, A.; Softley, T. P. *Chem. Phys. Lett.* **1986**, *106*, 315 (CO$_2$ laser, Doppler tuning)
	Yamada, C.; Kanamori, H.; Hirota, E. *J. Chem. Phys.* **1985**, *83*, 552 (IR diode)	CF[+]	Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1985**, *83*, 1437 (IR diode)
C[+]	Cooksy, A. L.; Blake, G. A.; Saykally, R. J. *Astrophys. J.* **1986**, *305*, L89 (FIR LMR)		Plummer, G. M.; Anderson, T.; Herbst, E.; De Lucia, F. C. *J. Chem. Phys.* **1986**, *84*, 2427 (mm and submm wave)
protonated rare gases			Gruebele, M.; Polak, M.; Saykally, R. J. *Chem. Phys. Lett.* **1986**, *125*, 165 (IR diode, $v = 0-7$)
HeH[+]	Tolliver, D. E.; Kyrala, G. A.; Wing, W. H. *Phys. Rev. Lett.* **1979**, *43*, 1719 (CO laser, Doppler tuning)	CCl[+]	Gruebele, M.; Polak, M.; Blake, G. A.; Saykally, R. J. *J. Chem. Phys.* **1986**, *85*, 6276 (IR diode)
	Carrington, A.; Buttenshaw, J.; Kennedy, R. A.; Softley, T. P. *Mol. Phys.* **1981**, *44*, 1233 (CO$_2$ laser, Doppler tuning)	NO[+]	Bowman, W. C.; Herbst, E.; De Lucia, F. C. *J. Chem. Phys.* **1982**, *77*, 4261 (mm and submm wave)
	Bernath, P.; Amano, T. *Phys. Rev. Lett.* **1982**, *48*, 20 (difference)		Ho, W. C.; Ozier, I.; Cramb, D. T.; Gerry, M. C. L. *J. Mol. Spectrosc.* **1991**, *149*, 559 (IR diode)
	Liu, D.-J.; Ho, W.-C.; Oka, T. *J. Chem. Phys.* **1987**, *87*, 2442 (IR diode)	PO[+]	Petrmichl, R. H.; Peterson, K. A.; Woods, R. C. *J. Chem. Phys.* **1991**, *94*, 3504 (MW)
	Blom, C. E.; Moller, K.; Filgueira, R. R. *Chem. Phys. Lett.* **1987**, *140*, 489 (IR diode)	SiH[+]	Davies, P. B.; Martineau, P. M. *J. Chem. Phys.* **1988**, *88*, 485 (IR diode)
(HeD[+])	Crofton, M. W.; Altman, R. S.; Haese, N. N.; Oka, T. *J. Chem. Phys.* **1989**, *91*, 5882 (difference)	SiF[+] (isotopes)	Petrmichl, R. H.; Peterson, K. A.; Woods, R. C. *J. Chem. Phys.* **1988**, *89*, 5434 (mm and submm wave, excited vibrational states)
NeH[+]	Wong, M.; Bernath, P.; Amano, T. *J. Chem. Phys.* **1982**, *77*, 693 (difference)		Akiyama, Y.; Tanaka, K.; Tanaka, T. *Chem. Phys. Lett.* **1989**, *155*, 15 (IR diode)
	Ram, R. S.; Bernath, P. F.; Brault, J. W. *J. Mol. Spectrosc.* **1985**, *113*, 451 (FTIR)	GeF[+]	Akiyama, Y.; Tanaka, K.; Tanaka, T. *Chem. Phys. Lett.* **1989**, *165*, 335 (IR diode)
	Liu, D.-J.; Ho, W.-C.; Oka, T. *J. Chem. Phys.* **1987**, *87*, 2442 (IR diode)		Tanaka, K.; Akiyama, Y.; Tanaka, T.; Yamada, C.; Hirota, E. *Chem. Phys. Lett.* **1990**, *171*, 175 (mm wave)
ArH[+]	Brault, J. W.; Davis, S. P. *Phys. Script.* **1982**, *25*, 268 (FTIR)		
(ArD[+])	Bowman, W. C.; Plummer, G. M.; Herbst, E.; De Lucia, F. C. *J. Chem. Phys.* **1983**, *79*, 2093 (MW)	linear molecular ions (diamagnetic)	
	Haese, N. N.; Pan, F.-S.; Oka, T. *Phys. Rev. Lett.* **1983**, *50*, 1575 (IR diode)	HCO[+]	Woods, R. C.; Dixon, T. A.; Saykally, R. J.; Szanto, P. G. *Phys. Rev. Lett.* **1975**, *35*, 1269 (MW)
	Johns, J. W. C. *J. Mol. Spectrosc.* **1984**, *106*, 124 (FTIR)		Anderson, T. G.; Gudeman, C. S.; Dixon, T. A.; Woods, R. C. *J. Chem. Phys.* **1980**, *72*, 1332 (MW, pressure broadening)
	Pan, F.-S.; Oka, T. *Phys. Rev.* **1987**, *A36*, 2297 (IR diode, diagnosis of discharge plasma)		Bogey, M.; Demuynck, C.; Destombes, J. L. *Mol. Phys.* **1981**, *43*, 1043 (mm wave, centrifugal distortion)
	Laughlin, K. B.; Blake, G. A.; Cohen, R. C.; Hovde, D. C.; Saykally, R. J. *Phys. Rev. Lett.* **1987**, *58*, 996 (tunable FIR, dipole moment)	(DCO[+])	Sastry, K. V. L. N.; Herbst, E.; De Lucia, F. C. *J. Chem. Phys.* **1981**, *75*, 4169 (mm and submm wave)
	Brown, J. M.; Jennings, D. A.; Vanek, M.; Zink, L. R.; Evenson, K. M. *J. Mol. Spectrosc.* **1988**, *128*, 587 (tunable FIR)		Woods, R. C.; Saykally, R. J.; Anderson, T. G.; Dixon, T. A.; Szanto, P. G. *J. Chem. Phys.* **1981**, *75*, 4256 (MW, structure)
	Filgueira, R. R.; Blom, C. E. *J. Mol. Spectrosc.* **1988**, *127*, 279 (IR diode)		Wooten, A.; Loren, R. B.; Snell, R. L. *Astrophys. J.* **1982**, *255*, 160 (radioastronomy)
	Liu, D.-J.; Ho, W.-C.; Oka, T. *J. Chem. Phys.* **1987**, *87*, 2442 (IR diode, color)		Van den Heuvel, F. C.; Dymanus, A. *Chem. Phys. Lett.* **1982**, *92*, 219 (tunable FIR)
	Gruebele, M.; Keim, E.; Stein, A.; Saykally, R. J. *J. Mol. Spectrosc.* **1988**, *131*, 343 (tunable FIR, potential function)		Gudeman, C. S.; Begemann, M. H.; Pfaff, J.; Saykally, R. J. *Phys. Rev. Lett.* **1983**, *50*, 727 (color, ν_1)
	Laughlin, K. B.; Blake, G. A.; Cohen, R. C.; Saykally, R. J. *J. Chem. Phys.* **1989**, *90*, 1358 (tunable FIR, dipole moment)		Amano, T. *J. Chem. Phys.* **1983**, *79*, 3595 (difference, ν_1)
	Geertsen, J.; Scuseria, G. E. *J. Chem. Phys.* **1989**, *90*, 6486 (theory, dipole moment)		Foster, S. C.; McKellar, A. R. W.; Sears, T. J. *J. Chem. Phys.* **1984**, *81*, 578 (IR diode, ν_3)
	Martin, P. A.; Guelachvili, G. *Phys. Rev. Lett.* **1990**, *65*, 2535 (FTIR)		Davies, P. B.; Hamilton, P. A.; Rothwell, W. J. *J. Chem. Phys.* **1984**, *81*, 1598 (IR diode, ν_3)
	Martin, P. A.; Guelachvili, G. *Chem. Phys. Lett.* **1991**, *180*, 344 (FTIR)		Foster, S. C.; McKellar, A. R. W. *J. Chem. Phys.* **1984**, *81*, 3424 (IR diode, ν_3)
KrH[+]	Johns, J. W. C. *J. Mol. Spectrosc.* **1984**, *106*, 124 (FTIR)		Davies, P. B.; Rothwell, W. J. *J. Chem. Phys.* **1984**, *81*, 5239 (IR diode, ν_2)
(KrD[+])	Warner, H. E.; Conner, W. T.; Woods, R. C. *J. Chem. Phys.* **1984**, *81*, 5413 (MW)		Kawaguchi, K.; Yamada, C.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1985**, *82*, 1750 (IR diode, ν_2)
XeH[+]	Rogers, S. A.; Braxier, C. R.; Bernath, P. F. *J. Chem. Phys.* **1987**, *87*, 159 (FTIR)	(DCO[+])	Kawaguchi, K.; McKellar, A. R. W.; Hirota, E. *J. Chem. Phys.* **1986**, *84*, 1146 (IR diode, ν_1)
(XeD[+])	Peterson, K. A.; Petrmichl, R. H.; McClain, R. L.; Woods, R. C. *J. Chem. Phys.* **1991**, *95*, 2352 (submm wave)		

TABLE VII (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
(DCO⁺)	Blake, G. A.; Laughlin, K. B.; Cohen, R. C.; Busarow, K. L.; Saykally, R. J. *Astrophys. J.* 1987, *316*, L45 (tunable FIR, $v_2 = 1$) Hirota, E.; Endo, Y. *J. Mol. Spectrosc.* 1988, *127*, 527 (MW)	HC₃NH⁺	Lee, S. K.; Amano, T. *Astrophys. J.* 1987, *323*, L145 (difference, ν_1) Kawaguchi, K.; Kajita, M.; Tanaka, K.; Hirota, E. *J. Mol. Spectrosc.* 1990, *144*, 451 (IR diode, ν_3)
	Liu, D.-J.; Lee, S.-T.; Oka, T. *J. Mol. Spectrosc.* 1988, *128*, 236 (IR diode, $2\nu_3 - \nu_3$ and $\nu_2 + \nu_3 - \nu_2$)	N₂H⁺	Thaddeus, P.; Turner, B. E. *Astrophys. J.* 1975, *201*, L25 (radioastronomy)
	Amano, T.; Nakanaga, T. *Astrophys. J.* 1988, *328*, 373 (difference, HCO⁺/HOC⁺ abundance ratio)		Saykally, R. J.; Dixon, T. A.; Anderson, T. G.; Szanto, P. G.; Woods, R. C. *Astrophys. J.* 1976, *205*, L101 (MW)
	Owrutsky, J. C.; Keim, E. R.; Coe, J. V.; Saykally, R. J. *J. Phys. Chem.* 1989, *93*, 5960 (color, ion beam, ν_1 intensity)		Szanto, P. G.; Anderson, T. G.; Saykally, R. J.; Piltch, N. D.; Dixon, T. A.; Woods, R. C. *J. Chem. Phys.* 1981, *75*, 4261 (MW)
	Keim, E. R.; Polak, M. L.; Owrutsky, J. C.; Coe, J. V.; Saykally, R. J. *J. Chem. Phys.* 1990, *93*, 3111 (color, ν_1 intensity)	(DN₂⁺)	Sastry, K. V. L. N.; Helminger, P.; Herbst, E.; De Lucia, F. C. *Chem. Phys. Lett.* 1981, *84*, 286 (mm and submm wave)
HOC⁺	Gudeman, C. S.; Woods, R. C. *Phys. Rev. Lett.* 1982, *48*, 1344; 1982, *48*, 1768 (MW)		Van den Heuvel, F. C.; Dymanus, A. *Chem. Phys. Lett.* 1982, *92*, 219 (tunable FIR)
	Blake, G. A.; Helminger, P.; Herbst, E.; De Lucia, F. C. *Astrophys. J.* 1983, *264*, L69 (mm and submm wave)		Gudeman, C. S.; Begemann, M. H.; Pfaff, J.; Saykally, R. J. *J. Chem. Phys.* 1983, *78*, 5837 (color, ν_1)
(DOC⁺)	Bogey, M.; Demuynck, C.; Destombes, J. L. *J. Mol. Spectrosc.* 1986, *115*, 229 (mm and submm wave)	(DN₂⁺)	Foster, S. C.; McKellar, A. R. W. *J. Chem. Phys.* 1984, *81*, 3424 (IR diode, ν_3)
	Nakanaga, T.; Amano, T. *J. Mol. Spectrosc.* 1987, *121*, 502 (difference, ν_1)	(DN₂⁺)	Nesbitt, D. J.; Petek, H.; Gudeman, C. S.; Moore, C. B.; Saykally, R. J. *J. Chem. Phys.* 1984, *81*, 5281 (difference, ν_1)
	Amano, T. *J. Mol. Spectrosc.* 1990, *139*, 457 (difference, $\nu_1 + \nu_2 - \nu_2$)	(DN₂⁺)	Sears, T. J. *J. Chem. Phys.* 1985, *82*, 5757 (IR diode, ν_2)
HCS⁺	Gudeman, C. S.; Haese, N. N.; Piltch, N. D.; Woods, R. C. *Astrophys. J.* 1981, *246*, L47 (MW)		Sears, T. J. *J. Opt. Soc. Am.* 1985, *B2*, 786 (IR diode, ν_2)
	Thaddeus, P.; Guélin, M.; Linke, R. A. *Astrophys. J.* 1981, *246*, L41 (radioastronomy)		Cazzoli, G.; Corbelli, G.; Degli Esposti, C.; Favero, P. G. *Chem. Phys. Lett.* 1985, *118*, 164 (MW, hfs)
	Irvine, W. M.; Good, J. C.; Schloerb, F. P. *Astron. Astrophys.* 1983, *127*, L10 (radioastronomy)	(DN₂⁺)	Owrutsky, J. C.; Gudeman, C. S.; Martner, C. C.; Tack, L. M.; Rosenbaum, N. H.; Saykally, R. J. *J. Chem. Phys.* 1986, *84*, 605 (color and IR diode, $\nu_1 + \nu_2 - \nu_2$)
	Bogey, M.; Demuynck, C.; Destombes, J. L.; Lemoine, B. *J. Mol. Spectrosc.* 1984, *107*, 417 (mm wave)		Owrutsky, J. C.; Keim, E. R.; Coe, J. V.; Saykally, R. J. *J. Chem. Phys.* 1989, *93*, 5960 (color, ion beam, ν_1 intensity)
	Davies, P. B.; Rothwell, W. J. *J. Chem. Phys.* 1985, *83*, 1496 (IR diode, ν_2)		Pursell, C. J.; Weliky, D. P.; Ho, W. C.; Takagi, K.; Oka, T. *J. Chem. Phys.* 1989, *91*, 7997 (color–MW double resonance)
	Rosenbaum, N. H.; Owrutsky, J. C.; Tack, L. M.; Saykally, R. J. *J. Chem. Phys.* 1985, *83*, 4845 (color, ν_1)		Nakanaga, T.; Ito, F.; Sugawara, K.; Takeo, H.; Matsumura, C. *Chem. Phys. Lett.* 1990, *169*, 269 (FTIR)
	Rosenbaum, N. H.; Owrutsky, J. C.; Saykally, R. J. *J. Mol. Spectrosc.* 1989, *133*, 365 (color, $\nu_1 + \nu_2 - \nu_2$, $\nu_1 + \nu_3 - \nu_3$, $\nu_1 + 2\nu_2 - 2\nu_2$, $\nu_1 + 3\nu_2 - 3\nu_2$, and ν_1)		Sasada, H.; Amano, T. *J. Chem. Phys.* 1990, *92*, 2248 (near-IR diode, $2\nu_2$)
HCNH⁺	Altman, R. S.; Crofton, M. W.; Oka, T. *J. Chem. Phys.* 1984, *80*, 3911 (difference, ν_2)		Ho, W. C.; Pursell, C. J.; Weliky, D. P.; Takagi, K.; Oka, T. *J. Chem. Phys.* 1990, *93*, 87 (color–MW double resonance)
(DCNH⁺)	Amano, T. *J. Chem. Phys.* 1984, *81*, 3350 (difference, ν_1)		Pursell, C. J.; Weliky, D. P.; Oka, T. *J. Chem. Phys.* 1990, *93*, 7041 (color–MW double resonance)
	Altman, R. S.; Crofton, M. W.; Oka, T. *J. Chem. Phys.* 1984, *81*, 4255 (difference, ν_1 and ν_2)		Keim, E. R.; Polak, M. L.; Owrutsky, J. C.; Coe, J. V.; Saykally, R. J. *J. Chem. Phys.* 1990, *93*, 3111 (color, ν_1 intensity)
	Bogey, M.; Demuynck, C.; Destombes, J. L. *J. Chem. Phys.* 1985, *83*, 3703 (mm and submm wave)		Havenith, M.; Zwart, E.; Meerts, W. L.; ter Meulen, J. J. *J. Chem. Phys.* 1990, *93*, 8446 (tunable FIR, dipole moment)
(isotopic species)	Amano, T.; Tanaka, K. *J. Mol. Spectrosc.* 1986, *116*, 112 (difference)	HBF⁺	Kawaguchi, K.; Hirota, E. *Chem. Phys. Lett.* 1986, *123*, 1 (IR diode, ν_3)
	Tanaka, K.; Kawaguchi, K.; Hirota, E. *J. Mol. Spectrosc.* 1986, *117*, 408 (IR diode, ν_4)		Cazzoli, G.; Degli Esposti, C.; Dore, L.; Favero, P. G. *J. Mol. Spectrosc.* 1986, *119*, 467 (MW)
	Ho, W.-C.; Blom, C. E.; Liu, D.-J.; Oka, T. *J. Mol. Spectrosc.* 1987, *123*, 251 (IR diode, ν_5)		Saito, S.; Yamamoto, S.; Kawaguchi, K. *J. Chem. Phys.* 1987, *86*, 2597 (MW)
	Kajita, M.; Kawaguchi, K.; Hirota, E. *J. Mol. Spectrosc.* 1988, *127*, 275 (IR diode, ν_3)		Cazzoli, G.; Degli Esposti, C.; Dore, L.; Favero, P. G. *J. Mol. Spectrosc.* 1987, *121*, 278 (MW)
	Liu, D.-J.; Lee, S.-T.; Oka, T. *J. Mol. Spectrosc.* 1988, *128*, 236 (IR diode, ν_3)	HNCCN⁺	Warner, H. E.; Amano, T. *J. Mol. Spectrosc.* 1991, *145*, 66 (difference, ν_1 and $\nu_1 + \nu_7 - \nu_7$)
HOSi⁺ (DOSi⁺)	Warner, H. E.; Fox, A.; Amano, T.; Bohme, D. K. *J. Chem. Phys.* 1989, *91*, 5310 (difference, ν_1)		Amano, T.; Scappini, F. *J. Chem. Phys.* 1991, *95*, 2280 (mm wave)
(DOSi⁺)	Moazzen-Ahmadi, N.; McKellar, A. R. W.; Warner, H. E.; Amano, T. *J. Chem. Phys.* 1989, *91*, 5313 (IR diode, ν_3)	CNC⁺	Fehér, M.; Salud, C.; Maier, J. P. *J. Chem. Phys.* 1991, *94*, 5377 (IR diode, ν_3 and hot bands from ν_2, $2\nu_2$, and $3\nu_2$)

TABLE VII (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
symmetric-top and spherical-top molecular ions			Maillard, J.-P.; Drossart, P.; Watson, J. K. G.; Kim, S. J.; Caldwell, J. Astrophys. J. **1990**, 363, L37 (IR astronomy, ν_2)
H_3^+ (D_3^+)	Shy, J.-T.; Farley, J. W.; Lamb, W. E., Jr.; Wing, W. E. Phys. Rev. Lett. **1980**, 45, 535 (CO laser, Doppler tuning)		Lee, S. S.; Ventrudo, B. F.; Cassidy, D. T.; Oka, T.; Miller, S.; Tennyson, J. J. Mol. Spectrosc. **1991**, 145, 222 (difference, $3\nu_2$)
	Oka, T. Phys. Rev. Lett. **1980**, 45, 531 (difference, ν_2)	CH_3^+	Crofton, M. W.; Kreiner, W. A.; Jagod, M.-F.; Rehfuss, B. D.; Oka, T. J. Chem. Phys. **1985**, 83, 3702 (difference, ν_3)
(H_2D^+)	Shy, J.-T.; Farley, J. W.; Wing, W. H. Phys. Rev. **1981**, A24, 1146 (CO laser, Doppler tuning)		Crofton, M. W.; Jagod, M.-F.; Rehfuss, B. D.; Kreiner, W. A.; Oka, T. J. Chem. Phys. **1988**, 88, 666 (difference, ν_3)
	Carrington, A.; Buttenshaw, J.; Kennedy, R. Mol. Phys. **1982**, 45, 753 (CO_2 laser, Doppler tuning)	H_3O^+	Begemann, M. H.; Gudeman, C. S.; Pfaff, J.; Saykally, R. J. Phys. Rev. Lett. **1983**, 51, 554 (color, ν_3)
(H_2D^+)	Warner, H. E.; Conner, W. T.; Petrmichl, R. H.; Woods, R. C. J. Chem. Phys. **1984**, 81, 2514 (MW)		Lemoine, B.; Destombes, J. L. Chem. Phys. Lett. **1984**, 111, 284 (IR diode, ν_2)
	Carrington, A.; Kennedy, R. A. J. Chem. Phys. **1984**, 81, 91 (CO_2 laser, Doppler tuning)		Haese, N. N.; Oka, T. J. Chem. Phys. **1984**, 80, 572 (IR diode, ν_2)
(H_2D^+)	Amano, T.; Watson, J. K. G. J. Chem. Phys. **1984**, 81, 2869 (difference, ν_1)		Bunker, P. R.; Amano, T.; Spirko, V. J. Mol. Spectrosc. **1984**, 107, 208 (molecular parameter determination)
	Watson, J. K. G.; Foster, S. C.; McKellar, A. R. W.; Bernath, P.; Amano, T.; Pan, F. S.; Crofton, M. W.; Altman, R. S.; Oka, T. Can. J. Phys. **1984**, 62, 1875 (difference and IR diode, ν_2)		Begemann, M. H.; Saykally, R. J. J. Chem. Phys. **1985**, 82, 3570 (color, ν_3)
			Liu, D.-J.; Haese, N. N.; Oka, T. J. Chem. Phys. **1985**, 82, 5368 (IR diode, ν_2)
(D_2H^+)	Lubic, K. G.; Amano, T. Can. J. Phys. **1984**, 62, 1886 (difference, ν_1)		Plummer, G. M.; Herbst, E.; De Lucia, F. C. J. Chem. Phys. **1985**, 83, 1428 (submm wave)
(H_2D^+)	Bogey, M.; Demuynck, C.; Denis, M.; Destombes, J. L.; Lemoine, B. Astron. Astrophys. **1984**, 137, L15 (MW)		Davies, P. B.; Hamilton, P. A.; Johnson, S. A. J. Opt. Soc. Am. **1985**, B2, 794 (IR diode, ν_2)
(H_2D^+)	Saito, S.; Kawaguchi, K.; Hirota, E. J. Chem. Phys. **1985**, 82, 45 (MW)	(D_3O^+)	Sears, T. J.; Bunker, P. R.; Davies, P. B.; Johnson, S. A.; Spirko, V. J. Chem. Phys. **1985**, 83, 2676 (IR diode, ν_2)
(H_2D^+)	Amano, T. J. Opt. Soc. Am. **1985**, B2, 790 (difference, ν_1)		Liu, D.-J.; Oka, T. Phys. Rev. Lett. **1985**, 54, 1787 (IR diode, ν_2)
(H_2D^+)	Phillips, T. G.; Blake, G. A.; Keene, J.; Woods, R. C.; Churchwell, E. Astrophys. J. **1985**, 294, L45 (radioastronomy)		Bogey, M.; Demuynck, C.; Denis, M.; Destombes, J. L. Astron. Astrophys. **1985**, 148, L11 (submm wave)
(H_2D^+)	Foster, S. C.; McKellar, A. R. W.; Peterkin, I. R.; Watson, J. K. G.; Pan, F. S.; Crofton, M. W.; Altman, R. S.; Oka, T. J. Chem. Phys. **1986**, 84, 91 (difference and IR diode, ν_2 and ν_3)		Liu, D.-J.; Oka, T.; Sears, T. J. J. Chem. Phys. **1986**, 84, 1312 (calculated ν_2 spectrum)
			Davies, P. B.; Johnson, S. A.; Hamilton, P. A.; Sears, T. J. Chem. Phys. **1986**, 108, 335 (IR diode, ν_2 hot bands)
	Pan, F.-S.; Oka, T. Astrophys. J. **1986**, 305, 518 (calculation of forbidden transitions)		Stahn, A.; Solka, H.; Adams, H.; Urban, W. Mol. Phys. **1987**, 60, 121 (color, ν_3)
(D_2H^+)	Foster, S. C.; McKellar, A. R. W.; Watson, J. K. G. J. Chem. Phys. **1986**, 85, 664 (IR diode, ν_2 and ν_3)		Gruebele, M.; Polak, M.; Saykally, R. J. J. Chem. Phys. **1987**, 87, 3347 (IR diode, ν_4)
	Carrington, A. J. Chem. Soc., Faraday Trans. 2 **1986**, 82, 1089 (CO_2 laser, Doppler tuning)		Verhoeve, P.; ter Meulen, J. J.; Meerts, W. L.; Dymanus, A. Chem. Phys. Lett. **1988**, 143, 501 (FIR laser sideband)
(D_3^+)	Watson, J. K. G.; Foster, S. C.; McKellar, A. R. W. Can. J. Phys. **1987**, 65, 38 (IR diode, ν_2)	($H_3^{18}O^+$)	Haese, N. N.; Liu, D.-J.; Oka, T. J. Mol. Spectrosc. **1988**, 130, 262 (IR diode, ν_2)
	Majewski, W. A.; Marshall, M. D.; McKellar, A. R. W.; Johns, J. W. C.; Watson, J. K. G. J. Mol. Spectrosc. **1988**, 128, 126 (IR emission)		Verhoeve, P.; Versluis, M.; ter Meulen, J. J.; Meerts, W. L.; Dymanus, A. Chem. Phys. Lett. **1989**, 161, 195 (FIR laser sideband)
(H_2D^+, D_2H^+)	Kozin, I. N.; Polyansky, O. L.; Zobov, N. F. J. Mol. Spectrosc. **1988**, 128, 126 (analysis)	(D_3O^+)	Petek, H.; Nesbitt, D. J.; Owrutsky, J. C.; Gudeman, C. S.; Yang, X.; Harris, D. O.; Moore, C. B.; Saykally, R. J. J. Chem. Phys. **1990**, 92, 3257 (difference, ν_3)
	Amano, T. Astrophys. J. **1988**, 329, L121 (difference, dissociative recombination rate)		Keim, E. R.; Polak, M. L.; Owrutsky, J. C.; Coe, J. V.; Saykally, R. J. J. Chem. Phys. **1990**, 93, 3111 (color, ν_3 intensity)
	Carrington, A.; McNab, I. R. Acc. Chem. Res. **1989**, 22, 218 (IR laser, Doppler tuning)		Ho, W. C.; Pursell, C. J.; Oka, T. J. Mol. Spectrosc. **1991**, 149, 530 (color, ν_3, ν_2 + $\nu_3 - \nu_2$)
	Drossart, P.; Maillard, J. P.; Caldwell, J.; Kim, S. J.; Watson, J. K. G.; Majewski, W. A.; Tennyson, J.; Miller, S.; Atreya, S. K.; Clarke, J. T.; White, Jr., J. H.; Wagner, R. Nature **1989**, 340, 539 (IR astronomy, $2\nu_2$)		Wooten, A.; Mangum, J. G.; Turner, B. E.; Bogey, M.; Boulanger, F.; Combes, F.; Encrenaz, P. J.; Gerin, M. Astrophys. J. **1991**, 380, L79 (radioastronomy)
	Oka, T.; Geballe, T. R. Astrophys. J. **1990**, 351, L53 (IR astronomy, ν_2)	SH_3^+	Nakanaga, T.; Amano, T. Chem. Phys. Lett. **1987**, 134, 195 (difference, ν_3)
	Bawendi, M. G.; Rehfuss, B. D.; Oka, T. J. Chem. Phys. **1990**, 93, 6200 (difference, $2\nu_2 - \nu_2$ and $\nu_1 + \nu_2 - \nu_1$)		Amano, T.; Kawaguchi, K.; Hirota, E. J. Mol. Spectrosc. **1987**, 126, 177 (IR diode, ν_2)
	Xu, L.-W.; Gabrys, C.; Oka, T. J. Chem. Phys. **1990**, 93, 6210 (difference, $2\nu_2$)		Saito, S.; Yamamoto, S.; Amano, T. Astrophys. J. **1987**, 314, L27 (MW)
(D_2H^+)	Polyansky, O. L.; McKellar, A. R. W. J. Chem. Phys. **1990**, 92, 4039 (analysis, ν_2 and ν_3)		Nakanaga, T.; Amano, T. J. Mol. Spectrosc. **1989**, 133, 201 (difference, ν_1 and ν_3)

TABLE VII (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
NH₄⁺	Crofton, M. W.; Oka, T. *J. Chem. Phys.* **1983**, *79*, 3157 (difference, ν₃)		Jefferts, K. B. *Phys. Rev. Lett.* **1969**, *23*, 1476 (radio frequency, hfs)
	Schäfer, E.; Begemann, M. H.; Gudeman, C. S.; Saykally, R. J. *J. Chem. Phys.* **1983**, *79*, 3159 (color, ν₃)	(HD⁺)	Wing, W. H.; Ruff, G. A.; Lamb, Jr., W. E.; Spezeski, J. J. *Phys. Rev. Lett.* **1976**, *36*, 1488 (IR laser, Doppler tuning)
	Schäfer, E.; Saykally, R. J.; Robiette, A. G. *J. Chem. Phys.* **1984**, *80*, 3969 (color, ν₃)	(HD⁺)	Ray, R. D.; Certain, P. R. *Phys. Rev. Lett.* **1977**, *38*, 824 (IR laser, hfs)
(NH₃D⁺)	Nakanaga, T.; Amano, T. *Can. J. Phys.* **1986**, *64*, 1356 (difference, ν₄)	(HD⁺)	Carrington, A.; Buttenshaw, J.; Roberts, P. G. *Mol. Phys.* **1979**, *38*, 1711 (IR laser, Doppler tuning)
(ND₄⁺)	Crofton, M. W.; Oka, T. *J. Chem. Phys.* **1987**, *86*, 5983 (difference, ν₃)		Carrington, A. *Proc. R. Soc. Lond.* **1979**, *A367*, 433 (IR laser, Doppler tuning)
	Polak, M.; Gruebele, M.; DeKock, B. W.; Saykally, R. J. *Mol. Phys.* **1989**, *66*, 1193 (IR diode, ν₄)	(HD⁺)	Carrington, A.; Buttenshaw, J. *Mol. Phys.* **1981**, *44*, 267 (IR laser, Doppler tuning)
	Keim, E. R.; Polak, M. L.; Owrutsky, J. C.; Coe, J. V.; Saykally, R. J. *J. Chem. Phys.* **1990**, *93*, 3111 (color, ν₃ intensity)	(HD⁺)	Carrington, A.; Buttenshaw, J.; Kennedy, R. A. *J. Mol. Struct.* **1982**, *80*, 47 (IR laser, Doppler tuning)
CH₃CNH⁺	Amano, T. *Astrophys. J.* **1988**, *330*, L137 (difference)	(HD⁺)	Carrington, A.; Buttenshaw, J.; Kennedy, R. A. *Mol. Phys.* **1983**, *48*, 775 (IR laser, Doppler tuning)
asymmetric-top molecular ions		(HD⁺)	Carrington, A.; Kennedy, R. A. *Mol. Phys.* **1985**, *56*, 935 (IR laser, Doppler tuning)
H₂F⁺	Schäfer, E.; Saykally, R. J. *J. Chem. Phys.* **1984**, *80*, 2973 (color, ν₁ and ν₃)	(HD⁺)	Carrington, A.; McNab, I. R.; Montgomerie, C. A. *J. Chem. Phys.* **1987**, *87*, 3246 (IR laser, Doppler tuning)
	Schäfer, E.; Saykally, R. J. *J. Chem. Phys.* **1984**, *81*, 4189 (color, ν₁ and ν₃)	(HD⁺)	Carrington, A.; McNab, I. R.; Montgomerie, C. A. *Chem. Phys. Lett.* **1988**, *149*, 326 (IR laser, Doppler tuning)
H₂Cl⁺	Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1986**, *85*, 6910 (IR diode, ν₂)	(HD⁺)	Carrington, A.; McNab, I. R.; Montgomerie, C. A. *Mol. Phys.* **1988**, *64*, 679 (IR laser, Doppler tuning)
	Saito, S.; Yamamoto, S.; Kawaguchi, K. *J. Chem. Phys.* **1988**, *88*, 2281 (MW)	(HD⁺)	Carrington, A.; McNab, I. R.; Montgomerie, C. A. *Chem. Phys. Lett.* **1988**, *151*, 258 (IR laser, Doppler tuning)
	Lee, S. K.; Amano, T.; Kawaguchi, K.; Oldani, M. *J. Mol. Spectrosc.* **1988**, *130*, 1 (difference, ν₁ and ν₃)	(HD⁺)	Carrington, A.; McNab, I. R.; Montgomerie, C. A. *Mol. Phys.* **1988**, *64*, 983 (IR laser, Doppler tuning)
HOCO⁺	Thaddeus, P.; Guélin, M.; Linke, R. A. *Astrophys. J.* **1981**, *246*, L47 (radioastronomy)	(HD⁺)	Carrington, A.; McNab, I. R.; Montgomerie, C. A. *Mol. Phys.* **1988**, *65*, 751 (IR laser, Doppler tuning)
	Bogey, M.; Demuynck, C.; Destombes, J. L. *Astron. Astrophys.* **1984**, *138*, L11 (submm wave)	(D₂⁺)	Carrington, A.; McNab, I. R.; Montgomerie, C. A. *Phys. Rev. Lett.* **1988**, *61*, 1573 (IR laser, Doppler tuning, 2pσᵤ-1sσ_g)
	Amano, T.; Tanaka, K. *J. Chem. Phys.* **1985**, *82*, 1045 (difference, ν₁)		Carrington, A.; McNab, I. R.; Montgomerie, C. A. *Chem. Phys. Lett.* **1989**, *160*, 237 (MW)
	Amano, T.; Tanaka, K. *J. Chem. Phys.* **1985**, *83*, 3721 (difference, ν₁)	(HD⁺)	Carrington, A.; McNab, I. R.; Montgomerie, C. A. *Mol. Phys.* **1989**, *66*, 519 (rf/IR double resonance)
(DOCO⁺)	Bogey, M.; Demuynck, C.; Destombes, J. L. *J. Chem. Phys.* **1986**, *84*, 10 (submm wave)	(D₂⁺)	Carrington, A.; McNab, I. R.; Montgomerie, C. A. Kennedy, R. A. *Mol. Phys.* **1989**, *67*, 711 (IR laser, Doppler tuning, 2pσᵤ-1sσ_g)
	Minh, Y. C.; Irvine, W. M.; Ziurys, L. M. *Astrophys. J.* **1988**, *334*, 175 (radioastronomy)		Carrington, A.; McNab, I. R.; Montgomerie, C. A. *Chem. Phys. Lett.* **1989**, *160*, 237 (MW)
	Bogey, M.; Demuynck, C.; Destombes, J. L.; Krupnov, A. *J. Mol. Struct.* **1988**, *190*, 465 (mm wave)	(HD⁺, D₂⁺)	Carrington, A.; McNab, I. R.; Montgomerie, C. A. Brown, J. M. *Mol. Phys.* **1989**, *66*, 1279 (MW)
HOCS⁺	Nakanaga, T.; Amano, T. *Mol. Phys.* **1987**, *61*, 313 (difference, ν₁)		Carrington, A.; McNab, I. R.; Montgomerie-Leach, C. A. *Mol. Phys.* **1991**, *72*, 735 (IR laser, Doppler tuning, rf/IR DR)
N₂OH⁺	Amano, T. *Chem. Phys. Lett.* **1986**, *127*, 101 (difference, ν₁)		
	Amano, T. *Chem. Phys. Lett.* **1986**, *130*, 154 (difference, comment)	He₂⁺ (³He⁴He⁺)	Yu, N.; Wing, W. H. *Phys. Rev. Lett.* **1987**, *59*, 2055 (CO laser, Doppler tuning)
	Bogey, M.; Demuynck, C.; Destombes, J. L.; McKellar, A. R. W. *Astron. Astrophys.* **1986**, *167*, L13 (mm wave)	(³He⁴He⁺)	Yu, N.; Wing, W. H.; Adamowicz, L. *Phys. Rev. Lett.* **1989**, *62*, 253 (CO laser, Doppler tuning)
(N₂OD⁺)	Bogey, M.; Demuynck, C.; Destombes, J. L. *J. Chem. Phys.* **1988**, *88*, 2108 (mm and submm wave)	OH⁺	Bekoy, J. P.; Verhoeve, P.; Meerts, W. L.; Dymanus, A. *J. Chem. Phys.* **1985**, *82*, 3868 (submm wave)
H₂COH⁺	Amano, T.; Warner, H. E. *Astrophys. J.* **1989**, *342*, L99 (difference)		Crofton, M. W.; Altman, R. S.; Jagod, M.-F.; Oka, T. *J. Phys. Chem.* **1985**, *89*, 3614 (difference)
C₂H₃⁺	Crofton, M. W.; Jagod, M.-F.; Rehfuss, B. D.; Oka, T. *J. Chem. Phys.* **1989**, *91*, 5139 (difference, ν₆)		
ArH₃⁺ (ArD₃⁺)	Bogey, M.; Bolvin, H.; Demuynck, C.; Destombes, J. L. *Phys. Rev. Lett.* **1987**, *58*, 988 (MW)	(OD⁺)	Gruebele, M. H. W.; Müller, R. P.; Saykally, R. J. *J. Chem. Phys.* **1986**, *84*, 2489 (FIR LMR)
(ArH₂D⁺, ArHD₂⁺, ArD₃⁺)	Bogey, M.; Bolvin, H.; Demuynck, C.; Destombes, J. L.; Van Eijck, B. P. *J. Chem. Phys.* **1988**, *88*, 4120 (MW)	(OD⁺)	Verhoeve, P.; Bekoy, J. P.; Meerts, W. L.; ter Meulen, J. J.; Dymanus, A. *Chem. Phys. Lett.* **1986**, *125*, 286 (FIR sideband)
radical ions			
H₂⁺	Jefferts, K. B. *Phys. Rev. Lett.* **1968**, *20*, 39 (radio frequency, hfs)		Liu, D.-J.; Ho, W.-C.; Oka, T. *J. Chem. Phys.* **1987**, *87*, 2442 (IR diode)
	Luke, S. K. *Astrophys. J.* **1969**, *156*, 761 (radio frequency)		

TABLE VII (Continued)

species[b]	ref (method and comment)	species[b]	ref (method and comment)
	Gruebele, M.; Keim, E.; Stein, A.; Saykally, R. J. *J. Mol. Spectrosc.* 1988, *131*, 343 (FIR LMR, color)	$C_2H_2^+$	Crofton, M. W.; Jagod, M.-F.; Rehfuss, B. D.; Oka, T. *J. Chem. Phys.* 1987, *86*, 3755 (difference)
SH[+]	Brown, P. R.; Davies, P. B.; Johnson, S. A. *Chem. Phys. Lett.* 1986, *132*, 582 (IR diode)	NH_3^+	Bawendi, M. G.; Rehfuss, B. D.; Dinelli, B. M.; Okumura, M.; Oka, T. *J. Chem. Phys.* 1989, *90*, 5910 (difference, ν_3)
(SD[+])	Zeitz, D.; Nelis, Th.; Urban, W. *Mol. Phys.* 1987, *60*, 255 (IR LMR)		Lee, S. S.; Oka, T. *J. Chem. Phys.* 1991, *94*, 1698 (IR diode, ν_2 and $2\nu_2 - \nu_2$)
	Hovde, D. C.; Saykally, R. J. *J. Chem. Phys.* 1987, *87*, 4332 (FIR LMR)	NH_2^+	Okumura, M.; Rehfuss, B. D.; Dinelli, B. M.; Bawendi, M. G.; Oka, T. *J. Chem. Phys.* 1989, *90*, 5918 (difference, ν_3)
	Civis, S.; Blom, C. E.; Jensen, P. *J. Mol. Spectrosc.* 1989, *138*, 69 (IR diode)		
NH[+]	Verhoeve, P.; ter Meulen, J. J.; Meerts, W. L.; Dymanus, A. *Chem. Phys. Lett.* 1986, *132*, 213 (FIR sideband)	H_2O^+	Strahan, S. E.; Mueller, R. P.; Saykally, R. J. *J. Chem. Phys.* 1986, *85*, 1252 (FIR LMR)
	Kawaguchi, K.; Amano, T. *J. Chem. Phys.* 1988, *88*, 4584 (difference)		Liu, D.-J.; Ho, W.-C.; Oka, T. *J. Chem. Phys.* 1987, *87*, 2442 (IR diode, rotation)
	Colin, R. *J. Mol. Spectrosc.* 1989, *136*, 387 (molecular constants)		Dinelli, B. M.; Crofton, M. W.; Oka, T. *J. Mol. Spectrosc.* 1988, *127*, 1 (difference, ν_3)
HF[+]	Hovde, D. C.; Schäfer, E.; Strahan, S. E.; Ferrari, C. A.; Ray, D.; Lubic, K. G.; Saykally, R. J. *Mol. Phys.* 1984, *52*, 245 (FIR LMR)		Brown, P. R.; Davies, P. B.; Stickland, R. J. *J. Chem. Phys.* 1989, *91*, 3384 (IR diode, ν_2 and $2\nu_2 - \nu_2$)
	Coe, J. V.; Owrutsky, J. C.; Keim, E. R.; Agman, N. V.; Hovde, D. C.; Saykally, R. J. *J. Chem. Phys.* 1989, *90*, 3893 (FIR sideband, ion beam)	**negative ions** C_2^-	Rehfuss, B. D.; Liu, D.-J.; Dinelli, B. M.; Jagod, M.-F.; Ho, W. C.; Crofton, M. W.; Oka, T. *J. Chem. Phys.* 1988, *89*, 129 (difference, $A^2\Pi_u - X^2\Sigma_g^+$)
	Hovde, D. C.; Keim, E.; Saykally, R. J. *Mol. Phys.* 1989, *68*, 599 (color)	NH[-] ([15]NH[-])	Miller, H. C.; Farley, J. W. *J. Chem. Phys.* 1987, *86*, 1167 (IR)
HCl[+]	Ray, D.; Lubic, K. G.; Saykally, R. J. *Mol. Phys.* 1982, *46*, 217 (FIR LMR)	OH^{-}	Owrutsky, J. C.; Rosenbaum, N. H.; Tack, L. M.; Saykally, R. J. *J. Chem. Phys.* 1985, *83*, 5338 (color)
(DCl[+])	Hinz, A.; Bohle, W.; Zeitz, D.; Werner, J.; Seebass, W.; Urban, W. *Mol. Phys.* 1984, *53*, 1017 (IR LMR)		Liu, D.-J.; Oka, T. *J. Chem. Phys.* 1986, *84*, 2426 (IR diode, rotation)
	Hinz, A.; Zeitz, D.; Bohle, W.; Urban, W. *Appl. Phys.* 1985, *B36*, 1 (IR LMR)		Rosenbaum, N. H.; Owrutsky, J. C.; Tack, L. M.; Saykally, R. J. *J. Chem. Phys.* 1986, *84*, 5308 (color)
(DCl[+])	Bohle, W.; Werner, J.; Zeitz, D.; Hinz, A.; Urban, W. *Mol. Phys.* 1986, *58*, 85 (IR LMR)	(OD[-])	Rehfuss, B. D.; Crofton, M. W.; Oka, T. *J. Chem. Phys.* 1986, *85*, 1785 (difference)
	Davies, P. B.; Hamilton, P. A.; Johnson, S. A. *Mol. Phys.* 1986, *57*, 217 (IR diode)		Liu, D.-J.; Ho, W.-C.; Oka, T. *J. Chem. Phys.* 1987, *87*, 2442 (IR diode, rotation)
($H^{35}Cl^+$, $H^{37}Cl^+$)	Lubic, K. G.; Ray, D.; Hovde, D. C.; Veseth, L.; Saykally, R. J. *J. Mol. Spectrosc.* 1989, *134*, 1 (FIR LMR)	SH[-]	Gruebele, M.; Polak, M.; Saykally, R. J. *J. Chem. Phys.* 1987, *86*, 1698 (color)
HBr[+]	Saykally, R. J.; Evenson, K. M. *Phys. Rev. Lett.* 1979, *43*, 515 (FIR LMR)		Elhanine, M.; Farrenq, R.; Guelachvili, G.; Morillon-Chapey, M. *J. Mol. Spectrosc.* 1988, *129*, 240 (FTIR)
(DBr[+])	Zeitz, D.; Bohle, W.; Nelis, Th.; Urban, W. *Mol. Phys.* 1987, *60*, 263 (IR LMR)		Benidar, A.; Farrenq, R.; Guelachvili, G.; Chackerian, C., Jr. *J. Mol. Spectrosc.* 1991, *147*, 383 (FTIR, intensity)
($H^{79}Br^+$, $H^{81}Br^+$)	Lubic, K. G.; Ray, D.; Hovde, D. C.; Veseth, L.; Saykally, R. J. *J. Mol. Spectrosc.* 1989, *134*, 21 (FIR LMR)	C_2H^-	Gruebele, M.; Polak, M.; Saykally, R. J. *J. Chem. Phys.* 1987, *87*, 1448 (IR diode, ν_3) [The assignment may not be final.]
(DBr[+])	Havenith, M.; Schneider, M.; Bohle, W.; Urban, W. *Mol. Phys.* 1991, *72*, 1149 (IR LMR)	HNO[-]	Miller, H. C.; Hardwick, J. L.; Farley, J. W. *J. Mol. Spectrosc.* 1989, *134*, 329 (IR)
N_2^+	Cramb, D. T.; Gerry, M. C. L.; Dalby, F. W.; Ozier, I. *Chem. Phys. Lett.* 1991, *178*, 115 (IR diode, A–X(2,5))	FHF[-] (FDF[-])	Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* 1986, *84*, 2953 (IR diode)
CO[+]	Dixon, T. A.; Woods, R. C. *Phys. Rev. Lett.* 1975, *34*, 61 (MW)		Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* 1987, *87*, 6838 (IR diode, ν_2 and ν_3)
	Sastry, K. V. L. N.; Helminger, P.; Herbst, E.; De Lucia, F. C. *Astrophys. J.* 1981, *250*, L91 (mm and submm wave)	ClHCl[-]	Kawaguchi, K. *J. Chem. Phys.* 1988, *88*, 4186 (IR diode, ν_3)
	Bogey, M.; Demuynck, C.; Destombes, J. L. *Mol. Phys.* 1982, *46*, 679 (mm wave)	N_3^-	Polak, M.; Gruebele, M.; Saykally, R. J. *J. Am. Chem. Soc.* 1987, *109*, 2884 (IR diode, ν_3)
	Van den Heuvel, F. C.; Dymanus, A. *Chem. Phys. Lett.* 1982, *92*, 219 (FIR sideband)		Polak, M.; Gruebele, M.; Peng, G. S.; Saykally, R. J. *J. Chem. Phys.* 1988, *89*, 110 (IR diode, $\nu_2 + \nu_3 - \nu_3$)
(isotopic species)	Piltch, N. C.; Szanto, P. G.; Anderson, T. G.; Gudeman, C. S.; Dixon, T. A.; Woods, R. C. *J. Chem. Phys.* 1982, *76*, 3385 (MW)	NCO[-]	Gruebele, M.; Polak, M.; Saykally, R. J. *J. Chem. Phys.* 1987, *86*, 6631 (IR diode, ν_3, $\nu_3 + \nu_1 - \nu_1$, $\nu_3 + \nu_2 - \nu_2$, and $\nu_3 + 2\nu_2 - 2\nu_2$)
	Bogey, M.; Demuynck, C.; Destombes, J. L. *J. Chem. Phys.* 1983, *79*, 4704 (mm wave)	NCS[-]	Polak, M.; Gruebele, M.; Saykally, R. J. *J. Chem. Phys.* 1987, *87*, 3352 (IR diode, ν_1, $\nu_1 + \nu_2 - \nu_2$, and $\nu_1 + \nu_3 - \nu_3$)
	Davies, P. B.; Rothwell, W. J. *J. Chem. Phys.* 1985, *83*, 5450 (IR diode)	NH_2^-	Tack, L. M.; Rosenbaum, N. H.; Owrutsky, J. C.; Saykally, R. J. *J. Chem. Phys.* 1986, *84*, 7056 (color, ν_1)
SO[+]	Amano, Takako; Amano, T.; Warner, H. E. *J. Mol. Spectrosc.* 1991, *146*, 519 (MW)		Tack, L. M.; Rosenbaum, N. H.; Owrutsky, J. C.; Saykally, R. J. *J. Chem. Phys.* 1986, *85*, 4222 (color, ν_1 and ν_3)
CO_2^+	Kawaguchi, K.; Yamada, C.; Hirota, E. *J. Chem. Phys.* 1985, *82*, 1174 (IR diode, ν_3)		
	Sears, T. J. *Mol. Phys.* 1986, *59*, 259 (IR diode, ν_2)		
	Frye, J. M.; Sears, T. J. *Mol. Phys.* 1987, *62*, 919 (IR diode)		

[a] For abbreviations for the method, see footnote *a* of Tables I–III.   [b] See footnote *b* of Table II.

The interaction Hamiltonian needs to be extended as follows:

$$H_{vibronic} = V_1 q\{exp[i(\theta - \alpha)] + exp[-i(\theta - \alpha)]\} +$$
$$V_2 q^2\{exp[i(\theta + 2\alpha)] + exp[-i(\theta + 2\alpha)]\} + ... \quad (19)$$

The molecule is assumed to have C_3 symmetry. The matrix will take the following form:

$$E \text{ state} \begin{bmatrix} E + (1/2)\omega q^2 + ... & h_1 q_- + h_2 q_+^2 + ... \\ h_1^* q_+ + h_2^* q_-^2 + ... & (1/2)\omega q^2 + ... \end{bmatrix} \quad (20)$$
$$A \text{ state}$$

where the harmonic frequency is again assumed to be the same for the two states for the sake of simplicity. The effective vibrational potential function is then given by

$$V_{eff}(E) = E + (1/2)\omega q^2 +$$
$$[|h_1|^2/E]q^2 + [|h_1 h_2|/E](q_+^3 + q_-^3) + ... \quad (21)$$

$$V_{eff}(A) =$$
$$(1/2)\omega q^2 - [|h_1|^2/E]q^2 - [|h_1 h_2|/E](q_+^3 + q_-^3) + ... \quad (22)$$

The first correction term modifies the harmonic frequency by $\pm 2|h_1|^2/E$, as in the case of a linear molecule. The second correction term is unique to the symmetric-top molecule. It gives the matrix elements $\Delta v = \pm 1$, ± 3; $\Delta l = \pm 3$. Hirota et al.[44] have shown that this term contributes to distorting the molecule in the first excited state of a degenerate mode in a nondegenerate electronic state. This can be easily visualized by calculating the average angular momentum associated with the degenerate mode p_α. A perturbation treatment of the second correction term gives the average value of p_α to be

$$\langle p_\alpha \rangle = 1 - 48(f_3/\omega)^2 \quad (23)$$

where $f_3 = |h_1 h_2|^2/E$. Hirota et al. applied this result to the NO_3 radical to explain some of anomalous features of the v_3 vibration-rotation spectra of this molecule. Weaver et al.[45] also have analyzed vibronic interaction in the NO_3 molecule to explain the unusual appearance of progression in v_4. The vibronic term they assumed is slightly different from the present one.

IV. Molecular Ions

Molecular ions have recently been attracting much interest. It is primarily because they play important roles in generating interstellar molecules. Two main mechanisms have been considered for the formation of interstellar molecules, chemical reactions on the surface of dust or grains and ion–molecule reactions. Although the former is indispensable in making hydrogen molecules from hydrogen atoms, most of the important subsequent processes have been ascribed to ion–molecule reactions. The low temperature and low density of interstellar media prohibit most chemical reactions which are quite common in laboratories from taking place in interstellar space; most of them have to pass an activation barrier and often need a third body to remove excess energy. These additional requirements are not met in interstellar space, leaving ion–molecule reactions as the most feasible path.

There were critical arguments for some time as to the possibility of recording high-resolution spectra of molecular ions. Because the intermolecular interactions

of molecular ions are so large, as represented by the Langevin cross section, the quantum mechanical uncertainty principle would make the spectra of molecular ions very broad. However, this apprehension turned out to be unnecessary. Woods and his workers[46,47] succeeded in observing the microwave spectra of the CO^+ and HCO^+ ions in 1975. The line widths they observed were not much different from those of ordinary molecules. Vibrational spectroscopy of molecular ions was initiated by Oka[48] in 1980, who observed the v_2 band of the H_3^+ ion using a difference-frequency laser system. Since then quite a large number of charged species have been detected by microwave and infrared laser spectroscopy, and their rotational and vibration-rotation spectra have been analyzed in detail, as summarized in Table VII.

Among molecular ions, the H_3^+ ion is a key species for formation of interstellar molecules. The most abundant molecule in interstellar space is the hydrogen molecule, and it may be ionized by cosmic rays to result in an ion, the hydrogen molecular ion H_2^+, which reacts readily with neutral hydrogen to produce H_3^+:

$$H_2 + H_2^+ \rightarrow H + H_3^+ \quad (24)$$

Then the H_3^+ ion reacts with other neutrals, M, with larger proton affinity than that of the hydrogen molecule to result in more complicated molecular ions:

$$H_3^+ + M \rightarrow MH^+ + H_2 \quad (25)$$
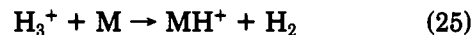
It is thus highly desirable to detect H_3^+ in interstellar space in order to substantiate the ion–molecule reaction mechanism. Much effort has thus been expended to detect H_3^+ in interstellar space. However, because this ion is an equilateral triangle symmetric-top molecule, it has no permanent dipole moment, making the ordinary rotational transitions forbidden. Therefore, attention has been paid to either rotational spectra of deuterated species, in particular of H_2D^+,[49] or to those of the normal species made allowed by a small dipole moment induced by centrifugal distortion and/or vibration–rotation interaction.[50a] Attempts have also been made to observe the infrared spectra of H_3^+.[50b] In spite of these efforts, no definite spectroscopic evidence has been obtained on the existence of interstellar H_3^+.

An interesting observation has, however, been reported recently. Drossart et al.[51] identified the overtone band $2v_2 \rightarrow 0$ of H_3^+ in the infrared spectra emitted from the auroral region of Jupiter. These infrared spectra were known for some time, but astronomers had thought that most of the observed lines were due to transitions of the hydrogen molecule in highly excited states. However, Watson noticed that many of the observed lines looked very similar to those observed by discharge in hydrogen,[52] and, in fact, he succeeded in assigning many of them to the overtone band of H_3^+. Subsequently Oka and Geballe and Maillard et al.[53] identified the v_2 fundamental band also in Jupiter. They tried to observe lines of the overtone band reported previously,[51] but found that most of them were missing. These observations indicate that the auroral region of Jupiter is very active and is drastically changing with time.

As Table VII indicates, most of the polyatomic ions so far investigated are so-called protonated ions, namely they are formed by attaching a proton to a stable molecule. We may almost always find neutral coun-

terparts which are isoelectronic and isovalent with the ions and are thus expected to have similar molecular structure. For example, HCO^+ may be compared with HCN and H_2Cl^+ with H_2S. Hirota[54] examined a few isoelectronic series of molecules and ions in terms of the Hellmann and Feynman theorem to disclose unique features of ions as compared with related neutrals. A series to which particular attention was paid consists of HBF^+, HBO, HCO^+, HCN, HNN^+, HNC, and HOC^+. Hirota found that the electronic force acting on hydrogen and the end atom increases as the series proceeds, whereas no definite trends are noticed for the central atom. Furthermore, the forces acting on H and the end atom are larger in ions than in isoelectronic neutrals. This sort of comparison is feasible for many classes of ion/neutral combinations and may clarify unique features of molecular ions.

Apart from the well-known high reactivity of ions, we may point out one molecular constant which contrasts ions with neutrals, namely the dipole moment, which is very difficult to obtain for ions. It is obvious that we cannot apply a static electric field to ions to measure their dipole moments. Saykally and his co-workers[55] thus employed a method which Townes et al.[56] devised to determine the absolute sign of the dipole moment. The method is based upon the rotational g factor derived from the Zeeman effect. The magnetic moment, or the g factor, induced by the rotational motion may be interpreted as being caused by an imbalance of positive and negative charges in the molecule, and is thus closely related with the dipole moment. The expression for the dipole moment of a linear ion is given by

$$\mu = -(eh/16\pi^2 M_p \Delta z)[(g'/B') - (g/B)] + (1/2)Qe\Delta z \tag{26}$$

where M_p denotes the mass of the proton, B the rotational constant, g the rotational g factor, z the coordinate along the molecular axis, and Qe the net charge of the ion. The prime indicates the quantity to be applied to an isotopic species. The last term of eq 26 is required only for the ion. Laughlin et al.[55] applied this method to ArH^+ and ArD^+ and derived the dipole moment to be 1.4 ± 0.4 D, where the rotational Zeeman effect was measured by far-infrared laser sideband spectroscopy with a magnetic field ranging from 800 to 4000 G. They have improved the technique by introducing a new magnet which delivered a field up to 6.2 kG. The value of the dipole moment was thus revised to 3.0 ± 0.6 D,[57] which may be compared with an ab initio result of 2.2 D.[58]

Havenith et al.[59] also carried out a similar measurement on the HN_2^+ ion, again using a far-infrared laser side-band spectrometer operated at 650 GHz. The g factor was measured for three isotopic species, $H^{14}N^{14}N^+$, $H^{14}N^{15}N^+$, and $H^{15}N^{14}N^+$. The dipole moment they thus determined for the normal species is 3.4 ± 0.2 D, which is in good agreement with an ab initio value, 3.37 D.[60]

There are a few exceptional protonated ions for which the corresponding neutrals either are completely missing or, if any, behave quite differently. Two of them should be mentioned here. One is protonated acetylene $C_2H_3^+$ and the other is ArH_3^+. Protonated acetylene has been predicted by ab initio calculations

to exist in two forms, a classical and a nonclassical form.[61] In the classical form two of the three hydrogen atoms are bonded to one carbon atom and the third hydrogen to the other carbon atom, something like in the vinyl radical, but with the energy minimum at a C_{2v} configuration. In contrast, the nonclassical form has one hydrogen in a bridged position, which is bonded to both carbon atoms equally, whereas the remaining two are attached one each to the carbon atoms. Crofton et al.[62] studied this ion using a difference-frequency laser spectrometer. They have found that the ion executes a very unique internal motion of large amplitude, namely three hydrogen atoms move around the two-carbon framework. The band they observed is the ν_6, i.e. the antisymmetric C–H stretching band at 3142.2 cm^{-1}. The nuclear spin statistical weight for $K_a = 1$ K-type doublets, the ground-state rotational constants derived from combination differences as compared with ab initio values, and the absence of other strong bands between 3300 and 2700 cm^{-1} all indicate that the species they detected is a nonclassical form of protonated acetylene. The large amplitude motion is quite complicated, if it is treated in a general way. Hougen[63] has proposed a one-dimensional model, in which the exchange motion of the protons is replaced by a rotation of a triangle made by the three protons, and the principal term in the potential function for this "internal" rotation is represented by a 6-fold term $V_6(1 - \cos 6\alpha)/2$. Crofton et al. found the tunneling splittings resolved in the upper state and determined the V_6 to be about 1400 cm^{-1}, but did not observe any splittings in the ground state, setting the lower limit of V_6 to 2100 cm^{-1}. They suspected that the upper state may be in resonance with a high-overtone state of the large amplitude motion, making the tunneling splittings observable only in this state.

The second example ArH_3^+ may be classified as a van der Waals complex. In the course of searching for CH_2D^+ rotational transitions, Destombes and his co-workers[64] detected a number of lines, which they later realized to be rotational transitions of a complex molecular ion. By studying the effects of deuterium substitution, they concluded that the ion consists of the H_3^+ moiety with Ar placed outside the H_3^+ triangle and on the line connecting the centroid of the triangle of H_3^+ and one of the hydrogens. Most of the observed lines were split by the internal rotation of the H_3^+ group. It is interesting to note that only Ar among rare gases forms this type of complex; Ne and He interact with H_3^+ too weakly to produce a complex, whereas Kr and Xe tend to be combined with H^+ rather than with H_3^+.

Although much smaller in number, about 10 anions have also been investigated. Here only one example is discussed in some detail. Kawaguchi and Hirota[65] observed a series of lines around 1850 cm^{-1}. It took them a long time to make assignment for these lines, and at last they identified the species responsible for these lines to be FHF^-, and assigned the observed lines to the ν_3, i.e. the antisymmetric H–F stretching band. An interesting feature of the generation of this ion is that fluorinated hydrocarbons are needed as precursors; a discharge in a mixture of hydrogen and fluorine did not give the ion. Kawaguchi and Hirota ascribed these observations to the fact that, because FHF^- is so stable, excess energy must be removed to stabilize the ion, and strong C–F bonds in fluorinated hydrocarbons com-

pensate for this large surplus of energy. The vibrational assignment of Kawaguchi and Hirota did not, however, yield a ν_3 frequency in agreement with ab initio calculations,[66] which predicted the frequency 300–500 cm^{-1} lower than the observed value. So Kawaguchi and Hirota[67] repeated the observation and found a band near 1300 cm^{-1}. The former ν_3 band was reassigned to the $\nu_1 + \nu_3$ band. An interesting feature of the vibrational spectrum of this ion is that the ν_2 bending frequency is very close to the ν_3 frequency; the unperturbed frequencies of the two modes are $\nu_2 = 1286.0284$ cm^{-1} and $\nu_3 = 1331.1502$ cm^{-1}, and the two bands were shown to interact strongly with each other. The ν_3 mode was found to be very anharmonic; the ν_2/ν_3 Coriolis interaction matrix element derived from the analysis of the spectrum is only 78% of the value calculated based on the ordinary second-order perturbation theory.

V. Carbon and Hydrocarbon Radicals of Small Size

A number of interesting transient species have recently been detected and investigated in detail by infrared laser and microwave spectroscopy. Here two types of such species are discussed: one is C_n molecules and the other hydrocarbon radicals.

A. C_n Molecules

Carbon plays very important roles in chemistry, astronomy, biology, and many other related fields, but only two of the molecules which consist of only carbon atoms had been detected in the gaseous phase until quite recently, namely C_2 and C_3. The former has long been known by its famous Swan band, whereas for the latter an electronic transition $\tilde{A}^1\Pi_u$–$\tilde{X}^1\Sigma_g^+$ at 4100–3400 Å was observed and analyzed to yield precise molecular parameters. Gausset et al.[68] examined the 4050 Å band of C_3 under high resolution and found the bending frequency to be very low, 63.7 cm^{-1}. They explained this low bending frequency to be caused by a large Renner–Teller effect. Matsumura et al.[69] and Kawaguchi et al.[70] succeeded in observing the ν_3 antisymmetric stretching band and associated hot and combination bands of C_3 by using infrared diode laser spectroscopy. They have shown that the molecule is quasilinear and the nonlinearity is exaggerated when the ν_3 mode is excited, whereas the ν_1 symmetric stretching band tends to keep the molecule linear. It is interesting to note that around the same time of the above laboratory experiments Hinkle et al.[71] identified the ν_3 band in the circumstellar spectrum of the carbon star IRC + 10216. Recently Schmuttenmaer et al.[72] observed seven transitions of the ν_2 bending fundamental band of C_3 directly using a far-infrared laser sideband spectrometer and analyzed the observed data together with those of Kawaguchi et al. to calculate the band origin to be 63.416 529 cm^{-1}. Spectroscopic measurements on C_3 have recently been very much extended by the technique of so-called SEP (stimulated emission pumping);[73,74] the vibrational levels are detected and assigned up to 8900 cm^{-1}.

Heath, Saykally, and their co-workers have recently been very successful in generating and monitoring small carbon molecules. They incorporated an ingeneous laser ablation technique to produce these molecules, in an infrared diode laser spectrometer with a slit nozzle.

TABLE VIII. Change of the Rotational Constants of C_3, C_5, C_7, and C_3O_2 with the Excitation of the Bending Mode^a

| molecule | $\Delta B/B(\%)$ | | ref |
	$v = 1$	$v = 2$	
C_3	2.1 (e)	4.9	70
	3.6 (f)		
C_5	0.36	0.70	75
C_7	9.3	22	76
C_3O_2	1.3 (e)	0.92	79
	0.72 (f)		

^{a}(e) and (f) denote the l-type doublet components.

By these means they succeeded in observing infrared spectra of C_5,[75] C_7,[76] and C_9.[77] The C_5 molecule has also been detected in the circumstellar spectrum of IRC + 10216.[78] These odd-carbon molecules all have a singlet Σ ground electronic state and are essentially linear molecules. However, C_7 shows anomalies which are similar to those observed for C_3. The band observed is the ν_4 antisymmetric C–C stretching band, and, when this mode is excited, the quasilinearity, or the nonlinearity is amplified. This behavior is in sharp contrast with those of C_5 and C_9, which behave as rigid linear molecules. Table VIII reproduces the change of the B rotational constant upon excitation of the bending mode determined for C_3, C_5, C_7, and C_3O_2; the last molecule has been known as a most typical quasilinear molecule.[79] It is seen from the table that C_3 and, in particular, C_7 exhibit a more conspicuous increase of the B rotational constant upon bending excitation than C_3O_2 does. This behavior of quasilinearity may be understood by examining the HOMO (highest occupied molecular orbital) character. In C_3 and C_7, the HOMO is π_u, and hence, when the molecule is bent, the parts of the HOMO of the same sign approach each other, favoring a bent structure. In contrast with these, the HOMO of C_5 and C_9 is π_g, and thus contributes to the resistance of the molecule to bending.[80]

It has been much more difficult to detect molecules consisting of an even number of carbon atoms. Ab initio calculations[81] and infrared and ESR spectroscopy[82] have indicated that these molecules exist in two forms; one has a linear triplet ground state and the other a cyclic singlet ground state, and they are nearly degenerate in energy. Recently Heath and Saykally[83] succeeded in observing the ν_3 band of C_4, by using the technique which they applied to odd-number carbon molecules. Although the spin splitting was resolved for only one line P(4), they confirmed the molecule to be paramagnetic and to have a $^3\Sigma_g^-$ ground state. A recent study on C_4 trapped in a low-temperature matrix[84] suggests the molecule to be slightly bent, but the gas-phase data of Heath and Saykally did not show any evidence for a bent structure of the molecule. No information has so far been obtained on the cyclic isomer.

The most exciting example among the C_n molecules would be C_{60}, buckminsterfullerene. However, this molecule is deliberately excluded from the present review article, because excellent reviews will be prepared by experts on C_{60}.

B. Hydrocarbon Radicals

The molecules to be discussed are expressed by the formula C_nH_m, and the cases $n = 2$ and 3 will be considered mainly.

For $n = 2$, m ranges from 1 to 6, but C_2H_4 ethylene and C_2H_6 ethane are excluded from the discussion. In addition, the $m = 1$ case CCH is already treated to some extent in section III.A and will not be considered further. Then essentially three cases remain to be considered: $m = 2$, 3, and 5. The first one normally exists as acetylene with a possible isomer vinylidene H_2CC, and much interest has been given to the latter. According to ab initio calculations,[85] the singlet H_2CC is not stable, but the triplet may be well bound. Recently Ervin et al.[86] carried out an extensive observation of the photoelectron spectra of $H_2C=C^-$ and succeeded in detecting the $\tilde{X}^1A_1$, $\tilde{a}^3B_2$, and $\tilde{b}^3A_2$ states of vinylidene. The lifetime of the singlet state against isomerization to acetylene was estimated to be 0.04–0.2 ps, and the isomerization energy to be 41–45 kcal mol^{-1}.

The $m = 3$ case is vinyl, which has been studied by Kanamori et al.[87] using infrared diode laser spectroscopy. The band they observed is mainly the CH_2 wagging mode, and thus, although they observed splittings in their spectra which are due to the tunneling motion of the $C-H_\alpha$ bond, they could obtain only an approximate value for the barrier height to the double minimum motion. It is certainly worthwhile to extend their measurements to the $C-H_\alpha$ rocking band, which is directly involved in the double-minimum motion. Previous studies[88] on vinyl and its derivatives indicated that the potential barrier to the double-minimum motion is much affected by the nature of substituents, as inferred from product analysis of chemical reactions which these molecules are involved in. Therefore, it is highly desirable to examine derivatives of vinyl by high-resolution spectroscopy.

An isomer of ethylene H_3CCH may be conceivable, but no evidence for its existence has so far been obtained, and it might be quite unstable. The $m = 5$ case is the ethyl radical, which Sears and his co-workers[89] have been investigating by using infrared diode laser spectroscopy. They have observed many spectral lines with good signal-to-noise ratio in the 500-cm^{-1} region, which are probably assigned to the CH_2 wagging band. The spectrum is complicated presumably because of internal rotation and also because of possible coupling between the internal rotation and the CH_2 "out-of-plane" bending (or wagging) motion.

For $n = 3$ we have many more varieties of molecules. Again we exclude the $m = 8$ case, namely propane. The $m = 1$ molecule CCCH has been known for some time, because its rotational spectrum has been observed in both the laboratory[90] and interstellar space.[91] An important contribution was brought about by Yamamoto et al.,[92,93] who detected cyclic-C_3H, first in the laboratory and then in interstellar space. The molecule was shown to have a B symmetry ground state. It may be interesting to speculate on the electronic structure of this molecule. Each carbon atom has four valence ($n = 2$) electrons, and seven of the 12 electrons are consumed to form three C–C and one C–H σ bonds and two to make a π bond, leaving three in nonbonding orbitals. The nonbonding orbitals which are lowest in energy would be those localized on the two carbon atoms that are not bonded to the hydrogen, and linear combination of the two nonbonding orbitals results in one a_1 and one b_2 orbital, the former being lower in energy. Therefore, the ground-state electronic configuration would be
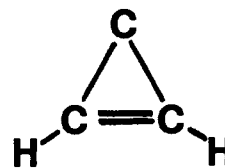

Figure 3. Cyclopropenylidene molecule.

$(a_1)^2(b_2)$, in accordance with the experimental observation.

For $m = 2$, a cyclic form has been shown to be the most stable, namely cyclopropenylidene shown in Figure 3. The rotational spectrum of this molecule was observed in space for the first time,[94] but its identification had to await a laboratory measurement 4 years later.[95] This molecule has a singlet ground state and is thus diamagnetic. Its dipole moment is as large as 3.43 D, as expected from its carbene-like structure.[96] A chain isomer of cyclopropenylidene is a molecule derived from the parent carbene CH_2 by replacing one of the two hydrogen atoms with the acetylenic group —$C\equiv C$—H, i.e. HC$\equiv$C—CH, but this molecule has not been identified. Quite recently, Thaddeus and his collaborators succeeded in detecting another isomer propadienylidene H_2CCC both in laboratory[97] and in space.[98] They also achieved identification of a related molecule butatrienylidene H_2CCCC.[99,100] Both molecules are planar and of C_{2v} symmetry. Although they are 0.63 and 1.9 eV higher in energy than cyclopropenylidene and diacetylene, respectively, the large dipole moment, 4.1 and 4.5 D for the two molecules respectively, certainly helped their identification by the Thaddeus group.[101]

Very few $m = 3$ molecules have been reported experimentally. Closs and Redwine[102] detected cyclic C_3H_3 in a matrix by using mainly ESR (electron spin resonance) spectroscopy. They found that the molecule deviates slightly from planarity. We may think of at least two interesting chain C_3H_3 radicals, namely propargyl HC$\equiv$C—CH$_2$ and allenyl HC$=$C$=$CH$_2$. Either one is in a metastable state. According to an ab initio calculation,[103a] the lowest form looks like propargyl, but is planar and of C_{2v} symmetry, whereas there are two excited states, both belonging to C_s symmetry, one of A$''$ symmetry and the other of A$'$ symmetry with excitation energies of 3.41 and 3.56 eV, respectively. Very recently Morter et al.[103b] succeeded in detecting the ν_1 C–H stretching band of propargyl by infrared laser kinetic spectroscopy. They generated the radical by flash photolysis of propargyl bromide or propargyl chloride at 193 nm.

We know at least three stable C_3H_4 molecules, namely cyclopropene, methylacetylene, and allene. The interconversion reactions among these three species have been discussed theoretically,[104] and the cyclopropene to methylacetylene rearrangement was predicted to proceed via singlet propenylidene H_3C—CH$=$C:.

There is a very important C_3H_5 radical that is allyl. Yamada[105] has observed a number of lines around 800 cm^{-1}, which are probably due to the CH_2 wagging band of b_1 symmetry. This molecule will have an electronic ground state of $^2A_2$ symmetry.[106] This can be understood by an argument similar to that applied to the cyclic-C_3H molecule.

Apart from a well-known stable molecule, cyclopropane, our knowledge on the $m = 6$ and 7 species are very limited. We certainly need more theoretical and experimental data.

Before leaving this section, a series must be mentioned, that is, the linear C_nH series. Up to the present the molecules of n up to 6 have been identified in laboratory and in interstellar space. There is an interesting story about the last member of the series C_6H. Because the even carbon members $m = 2$ and 4 of this series had been known to have a $^2\Sigma$ ground state, the first search for the rotational spectra of C_6H in laboratory was made assuming that the molecule was in a Σ ground state. The initial search failed. Then radioastronomers observed series of pairs of doublets,[107] which were found to be fitted nicely to the spectral pattern expected for a $^2\Pi$ molecule. The observed B rotational constant agreed well with that expected for C_6H. These observations suggest that the Π state gets lower and lower as the number of carbon atoms increases, passes the Σ state around C_4H, and becomes the ground state for C_6H. A similar interchange of the ground and lowest excited states has been reported for other series of molecules. One example is CN, SiN, GeN, etc. The Σ state is the ground state for CN and SiN, but will be replaced by the Π state for GeN and heavier molecules;[108] the Π state is already quite low, only 2032.4 cm^{-1} above the Σ ground state in SiN. Therefore, a very low-lying electronic Π state is expected for C_4H, but so far neither rotational nor vibration–rotation spectra of C_4H in such an excited electronic state have been observed, although Yamamoto et al.[109] reported rotational lines in excited bending states subjected to a very large Renner–Teller effect.

VI. Applications

Transient molecules play key roles in chemistry and related fields, and thus their high-resolution spectra will be useful or even indispensable to monitor these species in various environments. In the present section three such fields are considered: chemical reactions, astronomy, and plasmas.
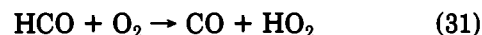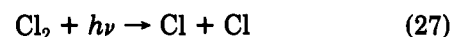
A. Chemical Reactions

As mentioned in the Introduction, most transient species were originally postulated in order to explain the mechanisms of chemical reactions. In the present days, we have various means to identify these species in reaction systems, and it is a prerequisite for the studies of chemical reactions to confirm the existence of all intermediate species. For unambiguous identification, high-resolution spectroscopy has the most potential and will remove many of the ambiguities encountered with low-resolution measurements.

Among such applications of high-resolution spectroscopy to chemical reactions, special mention should be made of kinetic spectroscopy. Although no precise definition is yet available for kinetic spectroscopy, it broadly means spectroscopy which allows us to get time-resolved information. Because of the limitation imposed by the quantum mechanical uncertainty principle, we may not expect to get very high time resolution, if we wish to keep high spectral resolution,

but it should be noticed that even millisecond or microsecond resolution provides us with invaluable information on many chemical reaction systems, provided that the spectral resolution permits us to unambiguously identify intermediate species.

Infrared and microwave kinetic spectroscopy obviously allows us to determine the populations in vibrational and rotational levels as functions of time. The time resolution normally achieved with conventional detection and amplification circuitry is about 0.3 μs,[110,111] which is by no means short, but is sufficient in many cases to observe phenomena that are not affected by intermolecular collisions in the gaseous phase. Strictly speaking, these spectroscopic techniques do not provide us with the population in each vibration–rotation and/or rotational level, but instead provide us the difference in population of the two levels between which the transition under observation takes place. However, in most cases it is possible to convert this population difference to the population in each level by making proper assumptions on the distribution as a whole.

One serious problem in applying high-resolution spectra of transient molecules to their diagnosis is how to convert the observed intensity into a population or abundance. For this purpose we certainly need the transition dipole moment. Because the spectra of transient species are weak and their production methods are frequently not compatible with Stark effect measurements, it is quite difficult to determine the permanent dipole moment, but it can be done at least in principle. The vibration–rotation transition dipole moment is much more difficult to obtain, and we must often be content with the values calculated using ab initio methods. However, in some favorable cases we may apply chemical methods. For example, Thrush and his co-workers[112,113] have demonstrated that the vibrational intensity of the HO_2 radical can be calibrated by using the following photochemical reactions:

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (27)$$

$$(I)\ Cl + CH_3OH \rightarrow HCl + CH_2OH \qquad (28)$$

$$CH_2OH + O_2 \rightarrow H_2CO + HO_2 \qquad (29)$$

$$(II)\ Cl + H_2CO \rightarrow HCl + HCO \qquad (30)$$

$$HCO + O_2 \rightarrow CO + HO_2 \qquad (31)$$

Namely, they photolyzed either a $Cl_2 + CH_3OH + O_2$ (I) or a $Cl_2 + H_2CO + O_2$ (II) mixture and measured the change in formaldehyde concentration, i.e. the amount formed or removed, respectively, simultaneously with the HO_2 line intensity using infrared diode laser spectroscopy. A similar technique was invented by Loh and Jasinski,[114] who calibrated the intensity of the SiH_3 radical using the following reactions:

$$CCl_4 + h\nu \rightarrow Cl + CCl_3 \qquad (32)$$

$$Cl + SiH_4 \rightarrow HCl + SiH_3 \qquad (33)$$
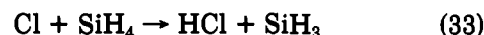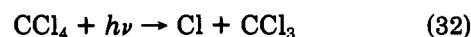
They measured the concentration of HCl formed, which could be set equal to that of SiH_3.

High-resolution infrared and microwave spectroscopy provides information on even finer details than molecular rotation. Kanamori et al.,[115] for example,

measured relative populations of three spin levels of SO in $X^3\Sigma^-$ generated by the 193-nm photolysis of SO_2 and found that F_2 levels were always less populated than F_1 and F_3 levels. The SO fragment seems to keep memory on the environment before the photolysis takes place.

Spectroscopy in longer wavelength regions is inferior in sensitivity to spectroscopy in the visible and ultraviolet regions. This drawback requires us to increase the pathlength, thereby sacrificing the spatial resolution. When the source of transient molecules is limited in space, this drawback will further reduce the sensitivity. Long pathlength is normally realized by using White-type multiple reflection. Then we may measure the abundance of transient molecules as a function of distance perpendicular to the plane made by the multipassed infrared beam.

In a reaction system as simple as $CH_3I + h\nu \rightarrow CH_3 + I$, we may specify all degrees of freedom to which available energy is allocated. For this example we may monitor a particular vibration–rotation transition of CH_3 by using infrared diode laser kinetic spectroscopy. If we know in which of the fine structure levels the iodine atom is prepared, we can calculate the nascent translational velocity of both CH_3 and I fragments and thus compare calculated Doppler line widths with the observed values. Suzuki et al.[116] showed that the observed signal of CH_3 corresponded mostly to that expected for the I* channel, namely the channel where iodine atoms are prepared in the upper fine structure level. They also found that for the first few microseconds CH_3 fragments were not subjected to any relaxation processes, namely they kept their nascent velocities, because the observed line width did not change for this time interval. In this way Suzuki et al. were able to derive the vibrational population distribution of methyl radicals without being affected by intermolecular collisions.

B. Astronomy

Spectroscopy and astronomy have collaborated for many years, and both sides have benefited very much through these collaborations. We may trace the origin of this tight relation back to last century (Fraunhofer in 1817). It was very natural to wonder what materials are responsible for the light of stars, and thus people started examining the light emitted from stars using spectrographs. In the beginning a few atoms (Ca, K, Fe, etc.) and atomic ions (Ca^+, Ti^+, etc.) were identified in interstellar space in this way. Then diatomic molecules CH and CN and a diatomic ion CH^+ followed.[117] After World War II radioastronomy was born; the hydrogen recombination line at 1420 MHz or 21 cm was detected in 1951,[118,119] and since then it has been employed extensively to diagnose the space. It was 1963 when the first radioastronomical observation of an interstellar molecule was made.[120] It is interesting to note that this first interstellar molecule is a radical, namely OH. In the early stage of radioastronomy, one had to tune the receiver to known frequencies measured for some stable molecules in the laboratory. Therefore, ordinary molecules such as NH_3 and H_2O were detected.

However, as the radiotelescope developed, the observation of interstellar molecules became much more extensive; radioastronomers did not need to limit the frequency range of observations, but could cover wide frequency regions at one time. As a result they discovered a number of lines which had no counterparts in laboratory measurements. The discovery of unexpected exotic molecules in interstellar space can easily be understood, if one considers the extreme conditions such as low temperature and low density there. At present, the number of molecules detected in interstellar space is approaching one hundred, and more than half of them are transient species under terrestrial conditions. The fraction of transient molecules has tended to become larger in recent years.

Molecules detected so far in interstellar space, but only short-lived under laboratory conditions are the following: CH, OH, CN, SO, CS, PN, AlF, AlCl, SiC, CP, SiN, CCH, CCCH, CCCCH, CCCN, CCCCCH, CCCCCCH, CCS, CCCS, CCO, CCCO, CCC, CCCCC, SiCCCC, HCO, HNO, C_3H_2, cyclic-C_3H, CH_2N, CH_2CN, H_2CCC, H_2CCCC, SiH_2, HCO^+, HCS^+, HN_2^+, HCO_2^+, SO^+, and $HCNH^+$. The high-resolution spectra of these molecules are of considerable significance in exploring various aspects of astronomical problems.

C. Plasmas

A plasma is a medium where many molecules are dissociated into smaller fragments and atoms and often further to ions and electrons. It normally emits light strongly so that it is difficult to diagnose molecular species present in the plasma by optical spectroscopic means. There are a large number of charged particles, which make it extremely difficult to apply charge-detecting techniques such as mass spectrometry and ion counting methods (e.g. MPI, multiphoton ionization). On the other hand, infrared spectroscopy may be applied to such media without much difficulty. One example is the application of infrared diode laser spectroscopy to a silane discharge plasma which has been employed to produce an amorphous silicon film (a-Si:H).

In this plasma the precursor silane will be dissociated into SiH_3, SiH_2, SiH, and Si, which may react with other species, mainly the precursor silane, to form molecules containing two or more silicon atoms. When the discharge current is large, charged species will also be produced. There had been controversy as to the roles of SiH_2 and SiH_3; some research groups thought SiH_2 to be the most important intermediate in the silane discharge plasma, whereas others gave more weight to SiH_3 than to SiH_2, but, because of the lack of reliable data, no definite conclusion had been drawn.

Goto and his co-workers[121-124] have successfully applied infrared diode laser spectroscopy to the silane discharge plasma to measure the abundances of the three species derived from the precursor SiH_4, namely they focused attention on SiH, SiH_2, and SiH_3. The infrared vibration–rotation bands $\nu = 1 \leftarrow 0$ and $2 \leftarrow 1$ of SiH had already been recorded extensively by several groups, and thus no further spectroscopic measurements were needed. In contrast with this species, the data on SiH_2 were very much limited; although the electronic bands in the visible region of this species had been well known and investigated in detail, no infrared spectrum was observed in the gaseous phase, only a matrix study had been carried out.[125] Therefore, Yamada et al.[126] started an infrared spectroscopic study of SiH_2; they observed and analyzed the

ν_2 band in the 10-μm region. Although they completed this study, they found the spectrum was a little too weak to be useful for a quantitative analysis of SiH_2 in a discharge plasma; nevertheless they could obtain some semiquantitative results with this spectrum. For SiH_3 Yamada and Hirota[127] had already investigated the ν_2 band, and this result could be readily employed for the quantitative analysis of SiH_3 radicals.

Itabashi et al. employed discharge modulation, i.e. they switched the discharge, either dc or rf, on and off and detected the signal synchronously with the discharge. They readily observed that the abundance of SiH_3 was an order of magnitude or more larger than that of SiH and SiH_2. This result is mainly ascribed to the difference in effective lifetime; both SiH and SiH_2 seem to react with the precursor SiH_4 quickly and thus their abundances are small. In contrast, SiH_3 is eliminated mainly by bimolecular processes, i.e. two SiH_3 radicals react to result in Si_2H_6 (recombination reaction) or SiH_2 + SiH_4 (disproportionation reaction), and, although the rate constant of this reaction is quite large, the effective rate is slow, making the abundance of this radical large. In fact, they showed that in a typical plasma condition the effective lifetime of SiH is in the millisecond range, which is to be compared with about 20 ms for the SiH_3 lifetime. Itabashi et al. analyzed the decay curve of the SiH_3 infrared absorption; they found that they needed two terms to fit the time variation, one proportional to the concentration and the other to the square of the concentration, and ascribed the linear term to the diffusion process and the quadratic term to the bimolecular reaction. By transferring an ab initio value of the transition dipole moment,[128] Itabashi et al. estimated the rate constant of the bimolecular reaction to be $(1.5 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Loh and Jasinski[114] remeasured this rate constant to be $(7.9 \pm 2.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} using the reaction mentioned in section VI.A.

Itabashi et al. further measured the abundance of SiH_3 as a function of the distance from the ground electrode, simultaneously with the growth rate of the a-Si:H film. They concluded that about half of the film growth occurred through SiH_3 diffusing to the surface of the substrate and the remaining growth through molecular species containing more than one silicon atom. A similar conclusion was obtained by Loh and Jasinski.

VII. Concluding Remarks and Future Developments

Because of its fundamental importance, high-resolution spectroscopy of transient molecules will further develop in the future. Some of the future trends are indicated in the text, and only the directions not mentioned in the text will be discussed below.

In recent years much attention has been paid to clusters, however the studies of clusters have been seriously hampered because of the lack of suitable methods of exploring their structures. Because most clusters in the gaseous phase are prepared in molecular beams, we may eliminate the Doppler broadening fairly easily. The problem is sensitivity; because the cluster size is normally very spread out, individual cluster species are not abundant. We need to improve the spectroscopic methods at hand or to devise new tech-

niques of much higher sensitivity. Another solution is to develop means to concentrate the abundance on one or a few cluster species in the sample.

We may speculate on much more challenging problems where high-resolution spectroscopy of "transient" species may be applied with good success. One might think that we do not need high resolution for condensed phases. However, there are at least a few examples known where high-resolution spectra were observed in a condensed phase. Recently Oka and his co-workers[129-132] have shown that hydrogen molecules in low-temperature matrices exhibited complicated rotational spectra in the infrared region. It would not be too absurd to speculate that some small transient molecules behave in a similar way. It would be more interesting if we could prepare some ionic species in the same way and observe their rotational and vibrational–rotational spectra in the condensed phase.

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