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Microwave Spectroscopy of Molecular Ions in the Laboratory and in Space [and Discussion]

R. C. Woods and R. J. Saykally

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Microwave spectroscopy of molecular ions in the laboratory and in space

By R. C. Woods

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, *U.S.A.*

The SO^+ molecular ion has been detected radioastronomically via the $J=\frac{5}{2}\rightarrow\frac{3}{2}$ rotational transitions, whose rest frequencies were determined by earlier laboratory spectroscopic studies. This ion was detected in seven interstellar sources, including both giant molecular clouds and a cold dark cloud, and thus appears to be very widely distributed in the Galaxy and to play an important role in interstellar chemistry. We have obtained rotational spectra of HCO^+ in a wide variety of vibrational states in three isotopic forms, leading to the equilibrium structural parameters that are consistent to a high degree in redundant determinations. These results will be compared to similar structures we have obtained for HCN and HNC. The high bending vibrational states observed for HCO^+ and HCN exhibit the effects of Stark broadening due to the electric fields present in the discharge plasmas. The effects observed for ions against neutrals will be compared, as will those for normal glow discharges against those for magnetically confined abnormal discharges.

INTRODUCTION

The applications of microwave spectroscopy to the study of molecular ions fall into three fairly distinct categories: precise determinations of geometrical and electronic structures of the ionic species, detection of ions in interstellar space by radioastronomy, and plasma diagnostics, i.e. probes of the ion's dynamical interaction with its environment. Because microwave transition frequencies can be measured with great accuracy and because they depend very directly on the moments of inertia of the species and thus its bond distances and angles, very accurate molecular structural information is potentially available from the technique. To fully exploit this potential, however, one must be able to obtain data in a sufficient number of excited vibrational states so that the effects of vibration–rotation interaction may be fully accounted for. Of all the bands of the electromagnetic spectrum the microwave region has proven especially suitable for detection of ions and other molecules in interstellar space, for two reasons. The regions where molecular species exist are very cold (so that the only upper states sufficiently excited to emit many photons are those of rotational transitions) and always associated with large amounts of dust (so that they are highly obscured or totally opaque to shorter-wavelength radiation but still transparent to microwave photons). In the laboratory plasma environment the shapes, widths, relative intensities and frequency displacements of microwave spectral transitions (as well as of those in other forms of high-resolution spectroscopy) can provide a great deal of information about the distribution of energy between vibration, rotation and translation in various species, and in the case of ions about the ion velocities, electric-field strengths, and plasma densities. The present discussion is in no way intended to be a comprehensive review of these areas, but rather will describe one topic in my recent research experience illustrating current efforts in each of the three categories.

RADIOASTRONOMY OF SO^+

In early 1985, our group was able to obtain a laboratory microwave spectrum of the SO^+ molecular ion (Warner *et al.* 1987) in its ground $^2\Pi_{\frac{1}{2}}$ state. We were able to measure five transitions that were sufficient to determine the effective rotational, centrifugal distortion, and lambda doubling constants and thus to predict any other rotational transitions in this $\Omega = \frac{1}{2}$ substate. Although the transitions were weak and there were numerous stronger nearby lines in any of the gas mixtures we used, the SO^+ transitions could be unambiguously identified by the very characteristic slow but observable Zeeman effect of a $^2\Pi_{\frac{1}{2}}$ state. The availability of this new laboratory data then introduced the possibility of a serious radioastronomical search for SO^+; this seemed particularly worthwhile because the ion–molecule models, e.g. that of Herbst & Leung (1986), predicted that SO^+ was one of the more abundant molecular ions in the interstellar medium, among those that had not been previously observed.

Thus the author entered into a collaboration with radioastronomers E. B. Churchwell, W. M. Irvine, and R. L. Dickman with the goal of detecting interstellar SO^+. This has been accomplished (Woods *et al.* 1987) in a series of four observing runs: three at the National Radio Astronomy Observatory, Kitt Peak, Arizona, and one at the Five College Radio Astronomy Observatory near Amherst, Massachusetts. The first three runs involved exclusively efforts on the $J = \frac{5}{2} \rightarrow \frac{3}{2}$ lambda doublet at 115.8 GHz and 116.2 GHz. Both of these doublet components were detected in six giant molecular clouds: SGRB2, ORION-A, NGC-7538, NGC-2264, DR21-OH, and W51. In figure 1 the resulting spectra obtained in the source DR21-OH are shown. Each spectrum involves an average of data from two different runs at NRAO (September 1985 and June 1986) with two different receivers. The figure also shows statistically smoothed curves based on a method of Brown *et al.* (1985) superimposed on the histogram plot of the raw data. This smoothing procedure has proved to be very useful in the SO^+ studies. In each of the six sources the intensities, Doppler shifts, and linewidths of the two lines were as similar as could be expected with the modest available signal:noise ratio. The actual values of the velocity shifts were also as expected for the individual sources. In addition we have barely detected one of the doublet components in the cold dark cloud L183.

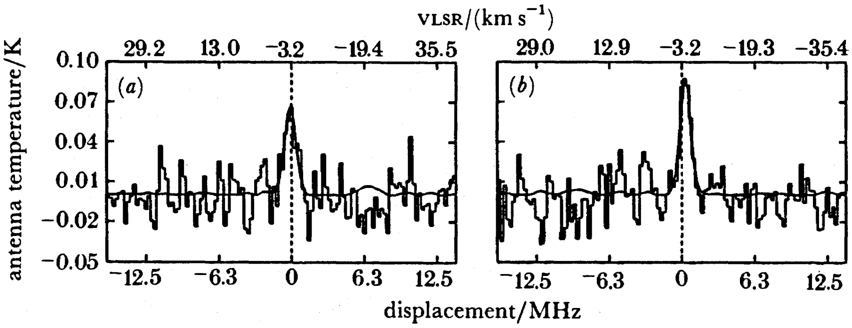

FIGURE 1. The $J = \frac{5}{2} \rightarrow \frac{3}{2}$ transitions of SO^+ in the giant molecular cloud DR21-OH. The smooth curve overlaying the spectrum of raw data is from the statistical analysis of Brown *et al.* (1985). (*a*) 115.8 GHz line; (*b*) 116.2 GHz line.

All this observational information taken together, we believe, provides a sufficient basis to conclude that the observed features are indeed caused by SO^+. Somewhat surprisingly, the intensities of the lines are comparable (0.05–0.10 K) in all of the seven sources. Detecting lines of this strength with currently available receivers requires several hours of signal averaging for each spectrum. Because we have detected signals for SO^+ in all seven of the sources in which we have looked, it appears that SO^+ is widely distributed in molecular clouds in the galaxy. To determine the overall abundance of SO^+ in the various sources reliably one must measure the degree of excitation, i.e. the rotational temperature, by measuring transitions with at least one more J value. The observed $J = \frac{5}{2} \rightarrow \frac{3}{2}$ emission intensities are sensitive only to the population in the $J = \frac{5}{2}$ rotational level. With this in mind our most recent observing run at NRAO (March 1987) involved efforts to observe the $J = \frac{11}{2} \rightarrow \frac{9}{2}$ transitions of SO^+ near 255 GHz. It turns out that these frequencies are more plagued with interfering lines than the earlier ones, and the results must certainly be considered preliminary at this point. We do appear to have detected SO^+ in NGC-7538, although very weakly. It appears that the $J = \frac{11}{2} \rightarrow \frac{9}{2}$ lines are quite weak and thus that the excitation temperatures are fairly low (less than or equal to about 20 K). Yet another series of observations is planned in the near future with the goal of further refining our estimate of the excitation. When overall SO^+ abundances are observationally available they can be compared to available theoretical models, and this will hopefully lead to further refinement of the latter and to a better understanding of interstellar sulphur chemistry. The SO^+ ion is only the second sulphur-containing molecular ion (after HCS^+ (Thaddeus *et al.* 1981)) to be observed in the interstellar medium. (It is also the only radical ion so far observed.)

EQUILIBRIUM STRUCTURE OF HCO^+

Substitution type (r_s) structures have been available for several years for HCO^+ (Woods *et al.* 1981), HNN^+ (Szanto *et al.* 1981), HOC^+ (Gudeman & Woods 1982) and the related neutral species HNC and HCN (Pearson *et al.* 1976). These structures are obtained from ground-vibrational-state data for the rotational constants or moments of inertia in several isotopic forms by using a simple well-known procedure (Kraitchman 1953). A more fundamental type of structure is the equilibrium (r_e) type, which gives the location of the actual minimum in the Born–Oppenheimer potential. It is the r_es that are predicted by *ab initio* quantum chemical calculations, and because the discrepancies of a few thousandths of an ångström (Å)† between r_e and r_s structures are comparable in magnitude to the uncertainties in the best *ab initio* structure predictions, an experimental r_e structure is essential for a full calibration of the accuracy of such a calculation. Experimentally r_es are gleaned from B_es that are determined from the effective rotational constants for each vibrational state via the equation

$$B_{v_1 v_2}{}^{l}{}_{v_3} = B_e - \alpha_1(v_1+\tfrac{1}{2}) - \alpha_2(v_2+1) - \alpha_3(v_3+\tfrac{1}{2}) + \gamma_{11}(v_1+\tfrac{1}{2})^2 + \gamma_{22}(v_2+1)^2 + \gamma_{33}(v_3+\tfrac{1}{2})^2 + \gamma_{12}(v_1+\tfrac{1}{2})(v_2+1) + \gamma_{13}(v_1+\tfrac{1}{2})(v_3+\tfrac{1}{2}) + \gamma_{23}(v_2+1)(v_3+\tfrac{1}{2}) + \gamma_{ll}\, l^2. \quad (1)$$

For simplicity the effects of l-type doubling and l-type resonance have been omitted from this equation, but they are fully accounted for in our analysis. At a minimum spectra in the ground vibrational state and one excited state of each of the three normal modes must be assigned. Then one can solve for B_e and the three αs with the γ parameters arbitrarily set to zero. We did this for HCO^+ several years ago (Gudeman 1982) by obtaining the (100), (001), and (02^00) satellite spectra for the normal isotopic species and also for $H^{13}CO^+$ and $HC^{18}O^+$.

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† 1 Å = 10^{-1} nm = 10^{-10} m.

Because there are only two bond distances, they can be determined independently by using any of the three possible isotope pairs. The results were disappointing because the three different values obtained for each bond length were not at all consistent, varying by as much as 0.01 Å. Considerable speculation on the origin of this inconsistency ensued. Exactly equivalent data were obtained for the isoelectronic molecule HCN, but in that case the three structure determinations appeared beautifully consistent. Was an ion in some critical way different from a neutral species? Was there an error in the HCO^+ data? Was there a perturbation between vibrational states in one of the isotopes? The last possibility eventually seemed most likely, particularly in the form of a possible third-order anharmonic resonance interaction between the observed (100) state and the (04^00) state.

We have now satisfactorily resolved these questions by obtaining a much more extensive set of vibrational satellite data for the three isotopic forms of HCO^+ (Gudeman *et al.* 1987). We have observed all three in the (100), (001), (01^10), (02^00), (02^20), (03^10), (03^30), (04^00), (002) and (01^11) states, so that γ_{22}, γ_{33}, γ_{23} and γ_{ll}, and an even higher-order parameter ϵ_{222}, can be determined in addition to B_e and the αs. In each state, centrifugal distortion parameters were measured. These are required to carry out the analysis of l-type resonance (DeLucia & Helminger 1977) mentioned earlier. Because the (04^00) satellites are found exactly where they are predicted from extrapolating the pattern of the lower bending states, we have eliminated the possibility of the suspected $(100)-(04^00)$ interaction in all three isotopic forms. In fact the earlier problems arose from the neglect of all the γ parameters in the previous treatment. Some of the γs are more isotope dependent in HCO^+ than they are in HCN. We now have B_es (taking into account αs but not γs) for HNC and the r_e structure in this case shows some of the same inconsistency problems that HCO^+ did. It seems now that HCN is somewhat fortuitous in working so well when only the α terms are used. The CO distance for HCO^+ is now consistent to 0.00002 Å and the CH distance to 0.0001 Å. A summary of r_e and r_s structures for HCO^+, HCN, HNC and HNN^+ (with the r_e structure of HNN^+ taken from the infrared work of Owrutsky *et al.* 1986) is given in table 1, where it can be seen that the $r_e - r_s$ values are fairly similar across this set of molecules.

TABLE 1. COMPARISON OF r_e AND r_s FOR ISOELECTRONIC SERIES

(Work at University of Wisconsin, except r_e for HNN^+. Numbers in parentheses indicate only the scatter (1σ) between determinations from various isotopic combinations. Realistic errors including systematic effects are larger.)

		$r(XY)/Å$	$r(XH)/Å$
HCO^+	r_e	1.104738 (23)	1.097247 (38)
	r_s	1.107211 (15)	1.092881 (35)
	$r_e - r_s$	0.0025	0.0044
HCN	r_e	1.153193 (16)	1.065825 (103)
	r_s	1.155461 (25)	1.063091 (33)
	$r_e - r_s$	0.0023	0.0027
HNC	r_e	1.168363 (226)	0.996959 (1450)
	r_s	1.172055 (7)	0.985884 (120)
	$r_e - r_s$	0.0037	0.0111
HNN^+	r_e[a]	1.097266 (92)	1.03359 (43)
	r_s	1.095415 (6)	1.031426 (56)
	$r_e - r_s$	0.0026	0.0022

[a] Data from Owrutsky *et al.* (1986). Errors in parentheses are quoted from that source.

STARK EFFECTS IN PLASMAS

The same vibrational satellite spectra of HCO^+ that have served to resolve the questions about the equilibrium structure have also provided some important new information on a dynamical property of the plasma, namely the prevailing electric-field strengths. Most microwave lines of molecular ions have rather slow Stark effects, so that the presence of the electric fields that are typically present in plasmas has a negligible impact on their appearance. Transitions involving degenerate or near-degenerate energy levels, e.g. vibrational satellites of linear molecules with high values of the bending quantum number v_2 and the vibrational angular-momentum quantum number l, however, have much faster Stark effects. Thus we have observed (in collaboration with G. Cazzoli) clear effects of the Stark perturbation in the (01^10), (02^20) and (03^30) states of HCO^+ (Conner *et al.* 1987). These include shifts of centre frequency, dramatic changes in peak amplitude, and increases in linewidth. We have carried out measurements in both normal DC glow discharges and in magnetically confined, abnormal glows, with magnetic fields of approximately 300 G† Furthermore, we have looked at the corresponding transitions in HCN in both types of discharge. (It is of course of interest to know if an ion and a neutral species experience the same electric field or not.)

Some preliminary results may be stated. The electric fields involved are not the macroscopic ones, but the microscopic fields from the local distribution of charged particles in the plasma. The macroscopic fields are entirely too small to explain the observed effects, especially in the abnormal discharge case, where the macroscopic fields have been shown to be very small. We have used the simple Holtsmark theory (Holtsmark 1919; Griem 1974) to estimate the distribution of electric fields for different plasma densities, and then used this along with a quasistatic approximation to simulate the observed spectral behaviour of the (02^20) or (01^10) transition. The observed effects can be at least qualitatively explained in this way, except in the case of an ion in the magnetically confined plasma. In that case, the effect is distinctly bigger than for the corresponding neutral, for reasons that are not yet understood. The (03^30) state presents a somewhat different case. Here the degeneracy is very much closer, so that the Stark effect is first order, rather than second. We find this satellite to be perturbed, but not as strongly as would be expected from a simulation of the above type (that would predict total obliteration for a line with such a fast Stark effect). This behaviour is probably caused by a breakdown in the validity of the quasistatic approximation because the frequencies of the fluctuations in the field are greater than the frequency separation betwen the interacting levels.

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† $1\ G = 10^{-4}\ T$.

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Discussion

R. J. SAYKALLY (*University of California, Berkeley, U.S.A.*). Professor Woods has reported the equilibrium structure of HCO^+ determined with incredibly high precision. It becomes questionable what the physical significance of such high precision structures really is, because subtle effects of electronic contributions to the moments of inertia become important at the 0.001 Å level. These require knowledge of both the rotational *g*-factor and the molecular potential surface to correctly account for them. At present this knowledge is not available for HCO^+, although we have recently published results for ArH^+ in which these corrections were made to obtain the adiabatic internuclear separation.

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R. C. WOOD. There are certainly some interesting theoretical problems involved in the determination of highly accurate molecular structures for polyatomic molecules, including some that are specific to ionized species. We cannot claim to have solved all these problems, but at least there are now some data of sufficient precision to make their consideration worthwhile. We are continuing to work on these details of the interpretation of the spectral data in terms of structure.