Infrared Diode Laser and Microwave Spectroscopy of Molecular Ions

E. Hirota

Phil. Trans. R. Soc. Lond. A 1988 **324**, 131-139
doi: 10.1098/rsta.1988.0006

Phil. Trans. R. Soc. Lond. A **324**, 131–139 (1988)
Printed in Great Britain

Infrared diode laser and microwave spectroscopy of molecular ions

By E. Hirota
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Some of the recent results on FHF^-, HBF^+, H_2Cl^+, H_3S^+, HCO^+, and DCO^+ are reviewed. The last two molecules are studied to detect the effect of the discharge electric field on l-type doublets in the $v_2 = 1$ and $v_2 = 2$ states. The Fermi interaction between ν_1 and $4\nu_2^0$ in DCO^+ is also discussed. These experimental results are followed by introduction of a simple procedure, based upon the Hellmann–Feynman theorem, that allows us to estimate the electron distributions in ions in comparison with those in related neutrals. Three isoelectronic series (1) NH^-, OH and FH^+, (2) HBF^+, HBO, HCO^+, HCN, HNN^+, HNC and HOC^+, and (3) NH_2^-, OH_2 and FH_2^+ are discussed by this method.

Introduction

Remarkable progress has recently been made on infrared (ir) and microwave (mw) spectroscopy of molecular ions. A number of new species such as protonated ions have been detected and their structures have been explored in detail. Still many interesting ions remain to be observed; examples include the protonated methane and the protonated formaldehyde. We have been trying to detect new ionic species by using either infrared diode laser spectroscopy or microwave spectroscopy, and have recently added a few examples to the list, as described in the present paper. There are a number of ionic species that have already been reported to exist, but still require further studies to unveil unique features of their properties. We have been making effort to study such ions by high-resolution spectroscopy. It may be worth mentioning that no established method has been reported to determine the dipole moment of the ion.

As more data are accumulated on molecular ions, we naturally wonder what really characterizes the charged species. The net charge of the ion plays important roles when it interacts with the environment. The ion is accelerated by the electric field, for example. It has an exceptionally large cross section, i.e. Langevin cross section for reactions with neutral molecules, the reactions known as the ion–molecule reactions, which proceed with almost no activation energy. The next question is how the net charge of the ions affects their properties when they are isolated in vacuum. A clue to answer this question may be provided by comparing molecular parameters of ions with those of isoelectronic neutrals. Recent extensive studies with infrared and microwave spectroscopy will make it possible to perform such comparisons, and so may open a new field in chemistry.

The first part of the present paper summarizes some of the recent results of my group, paying attention to unique features of each ion. The second part describes the development of a new method for estimating charge distribution in molecules and its application to three isoelectronic series of ions and neutrals.

RECENT INFRARED AND MICROWAVE SPECTROSCOPIC STUDIES OF MOLECULAR IONS

The FHF^- *ion*

Since we published the infrared spectrum of the ν_3 band of this ion (Kawaguchi & Hirota 1986*b*), no substantial progress has been made on this ion. One of the most important problems that still remains to be solved for this ion is that *ab initio* calculations cannot reproduce the observed band origin (K. Yamashita, personal communication); the calculated values are lower than the observed value by 300–500 cm^{-1}. We have attempted to detect the $FHCl^-$ ion, but have not been successful.

The HBF^+ *ion*

Based on our result on the ν_3 band (Kawaguchi & Hirota 1986*a*), the microwave spectrum of this ion has been observed by two groups (Cazzoli *et al.* 1986, 1987; Saito *et al.* 1987). The measurements were limited to the ground state, and the so-called r_s (substitution) structure was calculated. Vibrational satellites could, however, be observed without too much difficulty. They will allow us to derive not only the equilibrium structure, but also other interesting information on the ion, as demonstrated for HCO^+ and DCO^+ (see below). The ν_1 band has recently been observed by K. Kawaguchi & T. Amano (personal communication).

The H_2Cl^+ *ion*

We have observed and analysed the ν_2 band (Kawaguchi & Hirota 1986*c*). The molecular constants of the ion are very similar to those of an isoelectronic molecule H_2S. Kawaguchi & Amano (1987*b*) have recently extended the measurement to the ν_1, ν_3, and $2\nu_2$ bands; these modes were found to be coupled.

The H_3S^+ *ion*

Amano *et al.* (1987) have measured the ν_2 band by infrared diode laser spectroscopy combined with magnetic-field modulation. The ion was generated by a dry-ice-cooled hollow cathode discharge in a mixture of H_2S and H_2 with the partial pressures of 40 mTorr and 1 Torr,† respectively. Interest lay in whether the ν_2 band showed the effect of inversion, but the observed band did not exhibit any indication of splitting. The observed spectrum was analysed in a straightforward way, yielding rotational and centrifugal distortion constants. An anomalous feature of the derived parameters is that D_J, D_{JK}, and D_K change sign on going from the ground state to the ν_2 state. This was explained by the Coriolis interaction with ν_4, which was estimated to be about 160 cm^{-1} higher in frequency than ν_2. The ν_4 band has not been observed.

The HCO^+/DCO^+ *ions in excited vibrational states*

Kawaguchi *et al.* (1986) studied the ν_1 band of DCO^+ and found the α_1 constant to be about 100 MHz smaller than that estimated from those of related molecules. They ascribed this observation to the Fermi interaction between ν_1 and $4\nu_2^0$. However, no observation had been reported on the ν_2 state of DCO^+, preventing a quantitative analysis being done.

Hirota & Endo (1987) observed vibrational satellites of DCO^+ with a millimeter-wave

---

† 1 Torr ≈ 133.3 Pa.

spectrometer; the $J = 3 \leftarrow 2$, $4 \leftarrow 3$, and $5 \leftarrow 4$ transitions in the ν_2, $2\nu_2$, ν_1, and ν_3 states were recorded. The observed spectra were analysed by the procedure that De Lucia & Helminger (1977) developed to analyse the vibrational satellites of HCN. The $v_2 = 1$ spectra yielded the rotational constant B_{0110}, the centrifugal distortion constant D_{0110}, and the l-type doubling constant q_2, whereas the B and D constants in the 02^00 state and q_2^2/δ were derived from the $v_2 = 2$, $l = 0$ spectra, where δ denotes the vibrational energy difference between the $l = 2(\Delta)$ and $l = 0(\Sigma)$ sublevels in the $v_2 = 2$ manifold (the suffixes of B and D represent v_1, v_2, l, v_3).

The Fermi interaction between ν_1 and $4\nu_2^0$ was analysed in the following way. The two vibrational states were designated as a and b for the sake of simplicity, and to the unperturbed parameters of the two states were attached a superscript 0. Because the ν_1 satellites were well fitted to a $J(J+1)$ expansion, the unperturbed vibrational energy difference $\Delta E = E_{\mathrm{a}}^0 - E_{\mathrm{b}}^0$ and the interaction term W were assumed to be much larger than the rotational energy $B^0J(J+1)$. Then the perturbed rotational and centrifugal distortion constants were given by

$$B_{\mathrm{a}} = B_{\mathrm{a}}^0 - (1 - \Delta E/2\varDelta)\,(\tfrac{1}{2}\Delta B), \tag{1}$$

$$D_{\mathrm{a}} = D_{\mathrm{a}}^0 - (1 - \Delta E/2\varDelta)\,(\tfrac{1}{2}\Delta D) - (W^2/8\varDelta^3)\,\Delta B^2, \tag{2}$$

where $$\Delta B = B_{\mathrm{a}}^0 - B_{\mathrm{b}}^0,\ \Delta D = D_{\mathrm{a}}^0 - D_{\mathrm{b}}^0,$$

and $$\varDelta = [(\tfrac{1}{2}\Delta E)^2 + W^2]^{\frac{1}{2}}. \tag{3}$$

The B_{a}^0 constant, i.e. the unperturbed B constant in the ν_1 state, B_{1000}, was approximated by B_{000} minus the α_1 constant of DCN (325 MHz) (Winnewisser *et al.* 1971). This α_1 value is very close to the one that Kawaguchi *et al.* (1986) presumed to be the unperturbed α_1 constant of DCO^+ by reference to the data on related molecules. The B_{b}^0 constant was given by

$$B_{\mathrm{b}}^0 = B_{0400} = B_{0000} + 2(B_{0200} - B_{0000}) + 8\gamma_{22}. \tag{4}$$

The ground-state B constant, i.e. the first term of (4), was fixed at the value obtained by averaging those reported by Bogey *et al.* (1981) and Sastry *et al.* (1981) according to the uncertainties of their measurements. Other ground-state parameters were obtained in the same way. The present result was substituted in the second term of (4), whereas the third term was estimated by using the γ_{22} constant of DCN (1.094 MHz) (Winnewisser *et al.* 1971). The difference in B, ΔB, was thus obtained to be -729 MHz. The observed B_{a} constant thus led to $\Delta E/2\varDelta = 0.732$. The observed D_{a} constant was analysed in a similar way, where the change of the D constant on ν_1 excitation, β_1, was estimated to be -0.00051 MHz, which was the value reported for DCN (Winnewisser *et al.* 1971), and D_{b}^0 was calculated by the following equation:

$$D_{\mathrm{b}}^0 = D_{0000} + 4(D_{0110} - D_{0000}) + 3q_2^2/\delta. \tag{5}$$

The difference in D, ΔD, was thus calculated to be -0.32535 MHz, and the observed D_{a} constant yielded $W^2/\varDelta^3 = 0.731\ 10^{-6}\ \mathrm{MHz}^{-1}$, which, when combined with $\Delta E/2\varDelta = 0.732$ as obtained above, led to $\varDelta = 21.1$, $\frac{1}{2}\Delta E = 15.5$, and $W = 14.4\ \mathrm{cm}^{-1}$. The coefficients α and β of the unperturbed wavefunctions are given by

$$\alpha^2 = [\varDelta + \tfrac{1}{2}\Delta E]/2\varDelta \quad \text{and} \quad \beta^2 = [\varDelta - \tfrac{1}{2}\Delta E]/2\varDelta. \tag{6}$$

The above result $\Delta E/2\varDelta = 0.732$ corresponds to $\beta^2 = 0.134$ and to the unperturbed vibrational levels of $E_{\mathrm{a}}^0(\nu_1) = 2578.9\ \mathrm{cm}^{-1}$ and $E_{\mathrm{b}}^0\,(4\nu_2) = 2547.9\ \mathrm{cm}^{-1}$. The ν_2 frequency was estimated to be 660.2 cm^{-1} from the observed l-type doubling constant. Four times this value is 2641 cm^{-1}, which is higher than $E^0(4\nu_2)$ by about 100 cm^{-1}; this is of reasonable magnitude as an anharmonicity correction.

It is interesting to note that we observed only the $l = 0(\Sigma)$ component in the $2\nu_2$ spectrum, for both HCO^+ and DCO^+. This fact is explained by inhomogeneity of the discharge electric field in the hollow cathode, which broadens the $l = 2(\Delta)$ components. The effect of such Stark effect, although to much less extent, was also observed for the l-type doublet transitions of DCO^+ in the ν_2 state.

Charge distribution in molecular ions as compared with those in neutrals

The characteristics of ionic species may be clearly manifested if one compares the charge distribution in an ion with that of isoelectronic neutrals. In the present study, a simple procedure was developed that allowed us to estimate the charge distribution in a molecule from precise structure parameters provided by high-resolution spectroscopy.

The present method is based upon Born–Oppenheimer approximation and utilizes the Hellmann–Feynman theorem, allowing us to evaluate the force acting on a nucleus in molecule. If one designates the eigenvalue of the electronic ground state as U_0, the x component of the force acting on the αth nucleus is given by (Feynman 1939)

$$-(\partial U_0/\partial X_\alpha)_e = Z_\alpha e^2 \left\{ \left\langle 0 \left| \sum_j (x_j - X_\alpha)/r_{j\alpha}^3 \right| 0 \right\rangle - \sum_{\beta \neq \alpha} Z_\beta (X_\beta - X_\alpha)/R_{\alpha\beta}^3 \right\}, \tag{7}$$

where Z denotes the nuclear charge, x_j and X_α stand for the x coordinates of the jth electron and the αth nucleus, respectively, and $r_{j\alpha}$ and $R_{\alpha\beta}$ for the distances between j and α and α and β, respectively. The first term in the right-hand side of (7) may be simplified to

$$\bar{\rho}_{x\alpha} = \int \rho (x - X_\alpha)/r_\alpha^3 \, \mathrm{d}\tau, \tag{8}$$

where the electronic charge in a small volume $\mathrm{d}\tau$ at r_α from the αth nucleus is expressed as $\rho\,\mathrm{d}\tau$. We may refer to $\bar{\rho}_{x\alpha}$ as the electronic force. At the equilibrium, the electronic force is balanced by nuclear repulsion.

Application to diatomic species

Suppose the first nucleus with the charge Z_1 to be located at X_1 and the second nucleus of the charge Z_2 at X_2, with $R = X_2 - X_1$ denoting the equilibrium internuclear distance. The electronic force is given by $\bar{\rho}_{x1} = Z_2/R^2$ and $\bar{\rho}_{x2} = -Z_1/R^2$. Table 1 gives the numerical values of $\bar{\rho}$ for three isoelectronic molecules NH^-, OH and FH^+.

The NH^- ion has much smaller $|\bar{\rho}|$ than the other two molecules. This may be explained by the charge distribution in NH^- being more spread away from the centre of the molecule than in the other two. The last two molecules seem to have similar charge distributions, except that the charge is shifted toward the F atom in FH^+ a little more than toward the O atom in OH.

Table 1. Electronic force in diatomics

	NH^-	OH	FH^+
$R/\text{Å}$[a]	1.039[b]	0.96966[c]	1.0011[c]
$\bar{\rho}_{x1}/\text{Å}^{-2}$	6.48	8.51	8.98
$\bar{\rho}_{x2}/\text{Å}^{-2}$	−0.93	−1.06	−1.00

[a] 1 Å = 10^{-10} m = 10^{-1} nm.
[b] Neumark *et al.* (1985).
[c] Huber & Herzberg (1979).

Application to linear HXY *triatomics*

The three atoms H, X, and Y are numbered as 1, 2 and 3 and are placed on the *x*-axis from left to right in this order. The electronic force is then given by

$$\begin{aligned}\bar{\rho}_{x1} &= Z_2/R_{12}^2+Z_3/R_{13}^2,\\ \bar{\rho}_{x2} &= -Z_1/R_{12}^2+Z_3/R_{23}^2,\\ \bar{\rho}_{x3} &= -Z_1/R_{13}^2-Z_2/R_{23}^2.\end{aligned}$$

As shown in table 2, there are seven isoelectronic molecules of HXY type, of which four are positive ions and three neutral molecules. Unfortunately no negative ions of this series have been reported (examples are HBN^-, HCC^-, and HNB^-).

Table 2. Linear isoelectronic HXY triatomics

(Species in parentheses have not been reported.)

	X = Be	B	C	N	O	F
Y = Be	.	.	.	.	.	(HFBe)
B	.	.	.	.	(HOB)	(HFB^+)
C	.	.	.	HNC	HOC^+	
N	.	.	HCN	HNN^+		
O	.	HBO	HCO^+			
F	(HBeF)	HBF^+				

The electronic forces calculated for the seven molecules are plotted in figure 1, where the abscissa may be identified as $Z_X - Z_Y$. Structural data were taken from the following references: HBF^+ (Cazzoli *et al.* 1987); HBO (Kawashima *et al.* 1987); HCO^+ (Bogey *et al.* 1981); HCN (Winnewisser *et al.* 1971); HNN^+ (Owrutsky *et al.* 1986); HNC (Creswell & Robiette 1978); HOC^+ (Bogey *et al.* 1986).

It is easily seen from figure 1 that $\bar{\rho}_{x1}$ increases and $\bar{\rho}_{x3}$ decreases on going from left to right, whereas $\bar{\rho}_{x2}$ does not show any definite trend. This behaviour of $\bar{\rho}_{x1}$ and $\bar{\rho}_{x3}$ may be understood if one takes into account the electronegativities of the X and Y atoms. The second point is more important for the present problem. Both $\bar{\rho}_{1x}$ and $\bar{\rho}_{3x}$ show zigzags, namely, if one draws two curves passing through points for ions and neutrals, respectively, the one for ions is always larger in magnitude than the curve for neutrals. This means that more charge is located around the X atom in ions than in neutrals, when neighbouring species are compared. One might wonder if such zigzag behaviour is entirely ascribed to such behaviour in bond length, because the electronic force is derived from bond length. However, as shown in figure 2, this is not the case; although R_{X-Y} shows some zigzag behaviour in the central part of the figure, R_{HX} does not show any zigzags.

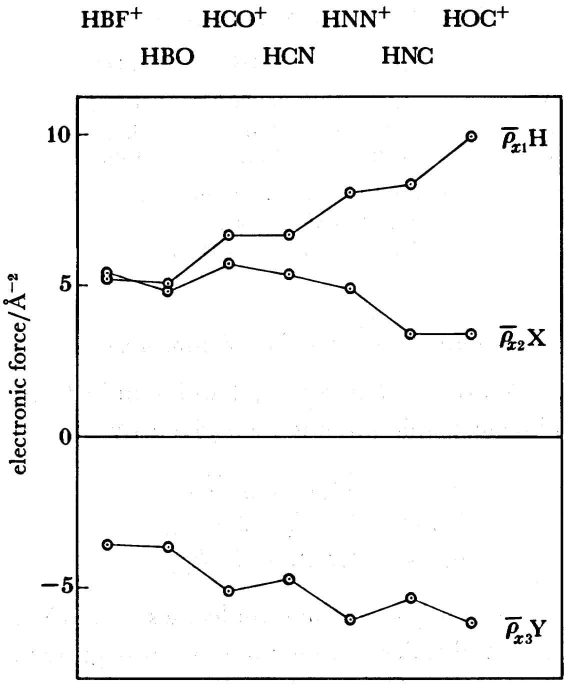

FIGURE 1. Electronic forces in linear HXY-type ions and neutrals; $\bar{\rho}_{x1}$, $\bar{\rho}_{x2}$ and $\bar{\rho}_{x3}$ represent the forces acting on H, X, and Y, respectively.

Application to bent C_{2v} XH_2*-type species*

Let us take the coordinate system as follows: the X atom is placed on the y-axis, whereas two hydrogens are located symmetrically about the y-axis. There are then three non-vanishing electronic forces:

$$\begin{aligned}\bar{\rho}_{x1} &= -\bar{\rho}_{x2} = [Z_1/4 \sin^2\theta + Z_3 \sin\theta]/R^2,\\ \bar{\rho}_{y1} &= \bar{\rho}_{y2} = Z_3 \cos\theta/R^2,\\ \bar{\rho}_{y3} &= -2Z_1 \cos\theta/R^2,\end{aligned}$$

where the atom numbers are 1 and 2 for hydrogens and 3 for X, and R and 2θ denote the X–H distance and the HXH angle, respectively. The electronic force was calculated for the third isoelectronic series NH_2^-, OH_2 and FH_2^+. Structural data were taken from the following references: NH_2^- (Tack *et al.* 1986); H_2O (Callomon *et al.* 1976); H_2F^+ (Schäfer & Saykally 1984). It is interesting to note that the angle 2 arctan $(\bar{\rho}_{y1}/\bar{\rho}_{x1})$ is larger than 2θ by 4.1°, 3.8°, and 3.0°, respectively, for the three molecules. The electronic force $[\bar{\rho}_{x1}^2 + \bar{\rho}_{y1}^2]^{\frac{1}{2}}$ acting on the hydrogen is compared with $\bar{\rho}_{x1}$ of the diatomics above mentioned in figure 3, where a similar comparison is also made for $\bar{\rho}_{y3}$ of XH_2 and $\bar{\rho}_{x2}$ of the diatomics. The similarities are very striking.

LCAO MO *interpretation of the electronic force*

It may be instructive to calculate the electronic force by using an LCAO MO (linear combination of atomic orbitals molecular orbital) for the wavefunction. Two atoms or nuclei called A and B are placed on the x-axis with the separation $R = X_B - X_A$. The LCAO MO is expressed

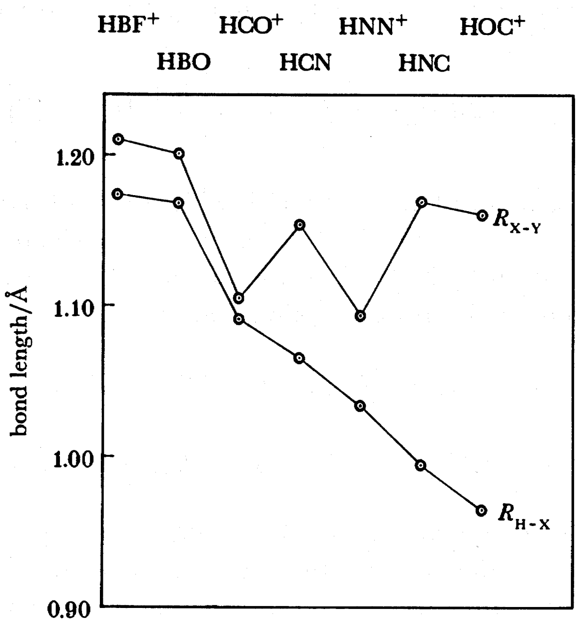

FIGURE 2. Bond lengths in linear HXY-type ions and neutrals.

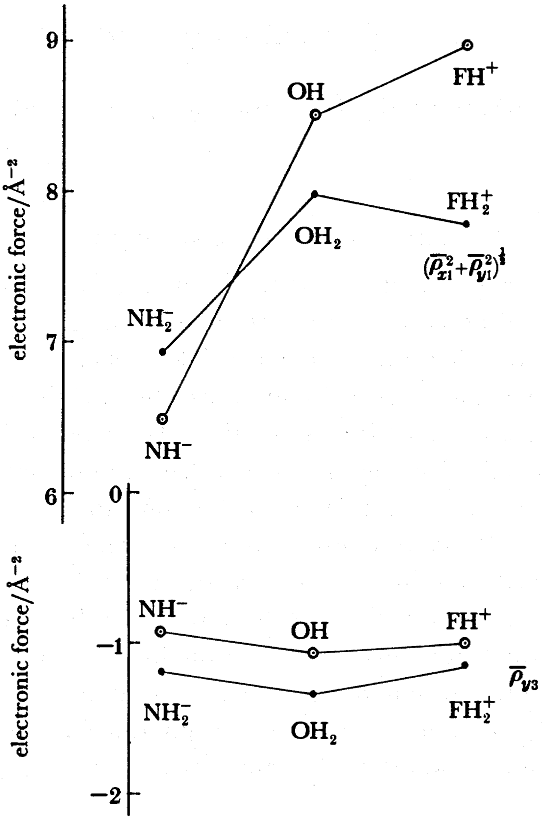

FIGURE 3. Electronic forces in XH-type diatomics and C_{2v} H_2X-type triatomics. The upper traces apply to hydrogens and the lower traces to X atoms.

as $\psi = c_A u_A + c_B u_B$ in terms of the atomic orbitals u_A and u_B. The electronic force is then given by

$$\bar{\rho}_{xA} = |c_A|^2 \int |u_A|^2 (x - X_A)/r_A^3 \, d\tau + 2Re[c_A^* c_B \int u_A^* u_B (x - X_A)/r_A^3 \, d\tau] + |c_B|^2 \int |u_B|^2 (x - X_A)/r_A^3 \, d\tau. \tag{9}$$

The first term of (9) is zero, because $|u_A|^2$ is symmetric with respect to inversion at X_A, whereas $x - X_A$ is antisymmetric. The second and third terms may be calculated analytically, if the atomic orbitals are approximated by hydrogenic wavefunctions. In the simplest case of both u_A and u_B being 1s, the second and third terms are given by

$$\int u_A u_B (x - X_A)/r_A^3 \, d\tau = (Z/a_0)^2 \exp(-D_1) \, D_1$$

and
$$\int u_B^2 (x - X_A)/r_A^3 \, d\tau = (Z/a_0)^2 [1/D_1^2 - \exp(-2D_1)\,(2 + 2/D_1 + 1/D_1^2)],$$

respectively, where $D_1 = ZR/a_0$, a_0 denoting the Bohr radius. The expressions are quite complicated if $Z_A \neq Z_B$ and if the principal quantum numbers of u_A and u_B are larger than 1. However, the functional forms of the second and third terms are proportional to

$$\int u_A u_B (x - X_A)/r_A^3 \, d\tau \propto \exp(-D_n) f_2(D_n)$$

and
$$\int u_B^2 (x - X_A)/r_A^3 \, d\tau \propto 1/R^2 - \exp(-2D_n) f_3(D_n),$$

respectively, where $D_n = ZR/na_0$ and $f_2(D_n)$ and $f_3(D_n)$ represent polynomial functions of D_n.

Discussion and conclusion

High-resolution spectroscopy has disclosed that a new group of molecules, i.e. molecular ions, exist and has been yielding very precise molecular constants of these species. Many more interesting examples will follow in future, and a new field of chemistry is expected to be opened. Because of their net charge, the ions are much more sensitive to interactions with environments than neutral molecules, as appreciated for some time. However, it has not been explored in detail how molecular ions differ from neutrals when they are isolated from environments. The present study aimed at proposing a simple way to respond to this problem. The information derived from this method on the charge distribution is not more than qualitative, but is based upon structural data derived from high-resolution spectroscopic experiments, which are very reliable. The method may be extended to utilize harmonic as well as anharmonic force constants and hyperfine constants, which are also obtainable from high-resolution data (see, for example, Salem 1963). In this connection it should be emphasized that an important molecular constant of ions, the dipole moment, is extremely valuable in estimating charge distribution in molecular ions, and much effort should be made to determine this constant experimentally.

REFERENCES

Amano, T., Kawaguchi, K. & Hirota, E. 1987 *J. molec. Spectrosc.* (In the press.)
Bogey, M., Demuynck, C. & Destombes, J. L. 1981 *Molec. Phys.* **43**, 1043–1050.
Bogey, M., Demuynck, C. & Destombes, J. L. 1986 *J. molec. Spectrosc.* **115**, 229–231.
Callomon, J. H., Hirota, E., Kuchitsu, K., Lafferty, W. J., Maki, A. G. & Pote, C. S. 1976 *Landolt–Börnstein tables*, new series, group II, vol. 7. Springer: Heidelberg.
Cazzoli, G., Degli Esposti, C., Dore, L. & Favero, P. G. 1986 *J. molec. Spectrosc.* **119**, 467.
Cazzoli, G., Degli Esposti, C., Dore, L. & Favero, P. G. 1987 *J. molec. Spectrosc.* **121**, 278–282.
Creswell, R. A. & Robiette, A. G. 1978 *Molec. Phys.* **36**, 869–876.
De Lucia, F. C. & Helminger, P. A. 1977 *J. chem. Phys.* **67**, 4262–4267.
Feynman, R. P. 1939 *Phys. Rev.* **56**, 340–343.
Hirota, E. & Endo, Y. 1987 *J. molec. Spectrosc.* (In the press.)
Huber, K. P. & Herzberg, G. 1979 *Molecular spectra and molecular structure, vol.* 4. *Constants of diatomic molecules.* New York: Van Nostrand.
Kawaguchi, K. & Hirota, E. 1986*a* *Chem. Phys. Lett.* **123**, 1–3.
Kawaguchi, K. & Hirota, E. 1986*b* *J. chem. Phys.* **84**, 2953–2960.
Kawaguchi, K. & Hirota, E. 1986*c* *J. chem. Phys.* **85**, 6910–6913.
Kawaguchi, K., McKellar, A. R. W. & Hirota, E. 1986 *J. chem. Phys.* **84**, 1146–1148.
Kawashima, Y., Endo, Y., Kawaguchi, K. & Hirota, E. 1987 *Chem. Phys. Lett.* **135**, 441–445.
Owrutsky, J. C., Gudeman, C. S., Martner, C. C., Tack, L. M., Rosenbaum, N. H. & Saykally, R. J. 1986 *J. chem. Phys.* **84**, 605–617.
Neumark, D. M., Lykke, K. R., Andersen, T. & Lineberger, W. C. 1985 *J. chem. Phys.* **83**, 4364–4373.
Saito, S., Yamamoto, S. & Kawaguchi, K. 1987 *J. chem. Phys.* **86**, 2597–2599.
Salem, L. 1963 *J. chem. Phys.* **38**, 1227–1236.
Sastry, K. V. L. N., Herbst, E. & De Lucia, F. C. 1981 *J. chem. Phys.* **75**, 4169–4170.
Schäfer, E. & Saykally, R. J. 1984 *J. chem. Phys.* **81**, 4189–4199.
Tack, L. M., Rosenbaum, N. H., Owrutsky, J. C. & Saykally, R. J. 1986 *J. chem. Phys.* **85**, 4222–4227.
Winnewisser, G., Maki, A. G. & Johnson, D. R. 1971 *J. molec. Spectrosc.* **39**, 149–158.

Note added in proof (8 *September* 1987). Kawaguchi & Hirota (submitted to *J. chem. Phys.*) have recently detected the ν_3 band of the FHF$^-$ ion at 1331.1507 (7) cm^{-1}, together with the ν_2 (1286.0284 (22) cm^{-1}) and $\nu_1 = \nu_3 - \nu_1$ (1265.6450 (19) cm^{-1}) bands. The former ν_3 band was reassigned to $\nu_1 + \nu_3$.