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Vibrational-state lifetime of ^{6}LiF[†]

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We report here a measurement of the lifetime of the first vibration state of ^{6}LiF. The experiment was carried out using an electric-resonance molecular-beam technique and yielded the result $\tau_{10} = 14.3^{+2.7}_{-2.1}$ msec. This value is smaller than the prediction of Rittner's model and also smaller than estimates using existing spectroscopic data.

INTRODUCTION

The electric-resonance molecular-beam method,[1] employed in the work reported here, has been a rich source of accurate data on electric dipole moments for alkali halides.[2] This information consists of values of the permanent electric dipole moments $\mu(r)$ for these molecules in given vibration states, that is, in the form of expectation values of $\mu(r)$.

Because excited molecular vibration states of alkali halides decay spontaneously to lower states via electric dipole radiation, a measurement of the lifetime for such a decay provides us with a measure of the square of the dipole moment derivative $(d\mu/dr)^2$.

Although rather feeble effects of vibrational decay may have been observed previously,[3,4] the authors know of no published work which reports the successful measurement of a vibrational lifetime for molecules free from interacting neighbors. To be sure, dipole moment derivatives are obtained from infrared spectroscopic data, but these data pertain to vapors under pressures which range from 1 Torr to many atmospheres. The mean time between collisions at such pressures is appreciably less than 1 μsec, whereas the natural radiative lifetime is measured in milliseconds. Thus the observed linewidths depend more on gas pressure than on the intrinsic properties of the molecule.

On the other hand, the molecular-beam electric-resonance technique applied to polar molecules enables us to measure natural radiative vibrational lifetimes because of the absence of interacting neighbors and because the relative populations in the beam of ground and excited vibration states can be determined as a function of beam velocity: faster molecules have less time in which to decay to lower vibrational states.

The following sections describe the application of the molecular-beam technique to the measurement of the natural radiative lifetime of the first vibration state in ^{6}LiF.

APPARATUS AND METHOD

This work was performed using the molecular-beam electric-resonance apparatus of overall length 2.5 m shown in Fig. 1. The LiF beam source was a Kusch-type[5] oven whose exit orifice, a circular opening of 0.035-in. diameter, was maintained at about 1300 °K at an operating pressure of about 0.2 Torr. The A and B quadrupole fields in Fig. 1 serve to select and focus beam molecules in the desired $J=1$, $M_J=0$ rotation state [(1, 0) molecules] according to principles which are adequately discussed elsewhere.[6] A focusing parameter p, valid in the quadratic Stark region, has been defined[7] as

$$p=\frac{V}{R^2}\left(\frac{2\mu^2A}{mv^2}\right)^{1/2}\left(\frac{J(J+1)-3M_J^2}{J(J+1)\,(2J-1)\,(2J+3)}\right) . \tag{1}$$

Here V is the applied rod voltage, $2R$ is the separation of like poles, while m and v are the molecular mass and velocity. The focal length f of a quadrupole lens can conveniently be written as

$$f=p^{-1}\cot(pl) , \tag{2}$$

where l is the length of the field.

The first term of the Stark energy $W(J,M_J)$ of a rigid rotator with permanent electric dipole moment μ and moment of inertia A in a field of electric intensity E is

$$W(J,M_J)=\frac{E^2\mu^2A}{\hbar^2}\left(\frac{J(J+1)-3M_J^2}{J(J+1)(2J-1)(2J+3)}\right)+\cdots , \tag{3}$$

and is shown in Fig. 2(a) for the $J=1$ and $J=2$ states. It can easily be seen that in an inhomogeneous field, some rotation states experience forces (indicated by the arrows) that tend to push molecules to weaker fields or toward the axis of a quadrupole lens.

The ball stop in Fig. 1 ensures that only the desired (1, 0) molecules can reach the detector.

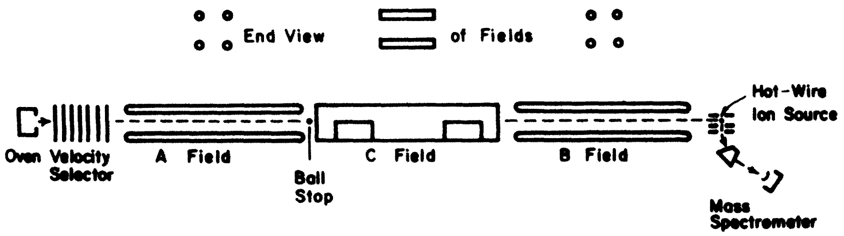

FIG. 1. Schematic diagram of electric-resonance molecular-beam apparatus with adaptations for vibrational lifetime measurements.

The construction of the uniform C field is shown in Fig. 3. The regions labeled I and II are where radiofrequency fields for the purpose of inducing transitions from the (1, 0) to the (1, ±1) states are superposed on the otherwise uniform field.

The velocity selector is similar to that described by Hostettler and Bernstein,[8] and beam detection was accomplished by a hot tungsten filament with ion-accelerator plates[9] as a source for a 60° mass spectrometer[10] at the end of which was placed an electron multiplier. The mass spectrometer was necessary to distinguish ^{6}Li from ^{7}Li ions.

Vibrational-state analysis of the ^{6}LiF beam can be carried out by inducing (1, 0) to (1, ±1) transitions in the C field [see Fig. 2(b)]. When such transitions occur, the resulting (1, ±1) molecules are defocused in the B field and do not strike the detector. Our method capitalizes on the fact that the energy difference ΔE between the (1, 0) and (1, ±1) states depends on vibration state. It is possible to induce transitions within a single and selectable vibration state, removing that state from the detected beam and thus obtaining a measure of vibrational population in the beam for any given vibration state.

By tuning the requisite radiofrequency applied to the C field, the relative populations in the beam of the ground and first vibration state may be obtained as shown in Fig. 4, where the variation in beam intensity is shown as a function of the applied radiofrequency. The changes in beam flux identified as S_0 and S_1 in Fig. 4 are used as relative measures of population in the ground and first excited vibration states. The doublet structure arises from hyperfine interaction and can be ignored. (S_1/S_0) can be obtained as a function of beam velocity by varying the rotation rate of the velocity selector. Equations (1) and (2) show that when the selected beam velocity is varied, the voltage V applied to the quadrupole fields must be varied accordingly.

We assume for the moment that each (1, 0) molecule which decays to a lower vibration state after leaving the oven source and before reaching the B field will be removed from the focused beam by virtue of the $\Delta J = 1$ selection rule. It is clear that the position of the farthest point from the oven that a molecule may reach and still be removed

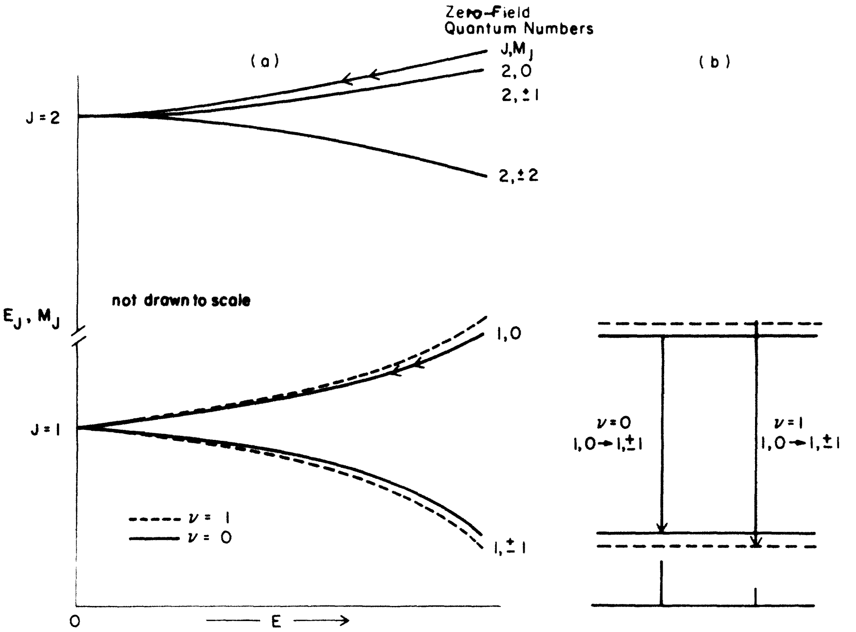

FIG. 2. (a) Variation of rotational levels, E_{J,M_J}, as a function of electric field intensity E. The energy difference between the $v=1$ and $v=0$ levels is field dependent and nonzero at $E=0$. (b) Vertical arrows represent indicated transitions occurring within the C field. Relative intensity is indicated by vertical lines.

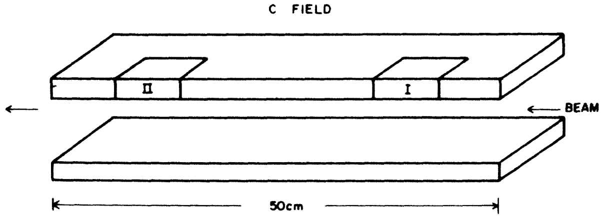

FIG. 3. The C field showing the transition sections I and II in the tip plate. An rf voltage is applied between a transition section and the top plate, which is at ground potential.

from the beam when it decays must be between the beginning and the end of the B field. If the beam and detector were of infinitesimal width, then the beginning of the B field would be the appropriate point. Considerations of beam width and geometry indicate that the center of the B field should serve as the critical point some 180 cm from the oven. Since the B field is 40 cm long, reasonable limits on the effective length of the apparatus are ±10 cm. Thus the effective length is 180±10 cm.

The relative population R of the first to ground vibration states measured at the detector becomes

$$R = R_s e^{-t/\tau} = R_s e^{-L/v\tau} = S_1/S_0 . \tag{4}$$

Here R_s is the relative population of adjacent vibration states in the oven source, t is the time of flight over the distance $L = 180 \pm 10$ cm, v is the selected beam velocity, and τ is the vibrational lifetime.

We may assume R_s is constant over the time of the measurements because of the high stability of the monitored oven temperature. Of equal importance is our assumption that the LiF beam velocity is not correlated to vibration state and that R_s above is independent of velocity. We feel that this is a valid assumption for several reasons. The existence of such a correlation has never been demonstrated for ovens operating under similar conditions, whereas thermal equilibrium has been amply demonstrated[11] for ovens operating even at significantly higher pressure. In the specific case of LiF beams, the vibration state distribution has been shown[3] to be consistent with an equilibrium distribution for ovens at similar and somewhat higher pressure. Furthermore, beams of sodium and potassium atoms produced in ovens identical to the one used here for LiF and operating at the same pressure displayed velocity distributions whose maxima were in excellent agreement with a modified Maxwellian distribution employing the measured oven temperatures. The best demonstration that a correlation between velocity and vibration is not present would consist of a study of lifetime as a function of oven pressure. Such a study was not feasible because beam intensity was at a premium. However, we were able to vary oven pressure more than a factor of 3 with no obvious effects on the resulting lifetime.

To the extent that the assumptions above are valid and providing there are no growth terms for either $v=0$ or $v=1$ populations, the vibrational lifetime can easily be obtained from Eq. (4), since R is the measured ratio S_1/S_0. A plot of the absolute values of $\ln(S_1/S_0)$ vs $-1/v$ has a slope L/τ from which τ is readily obtained (see Fig. 5).

The validity of the assumptions that all vibrationally decaying molecules are removed from the beam, that there are now growth terms, and that the measured ratio S_1/S_0 adequately represents the ratio R requires discussion.

The first assumption—that all $v=1$ molecules which decay after entering the A field are removed from the beam—is a good one but not strictly true for molecules decaying in the presence of a strong electric field. The effect of the field is to mix adjacent rotational states via the $\vec{\mu}\cdot\vec{E}$ matrix elements. Consequently, the admixed parts of a so-called (1, 0) $v=1$ state can decay to the princi-

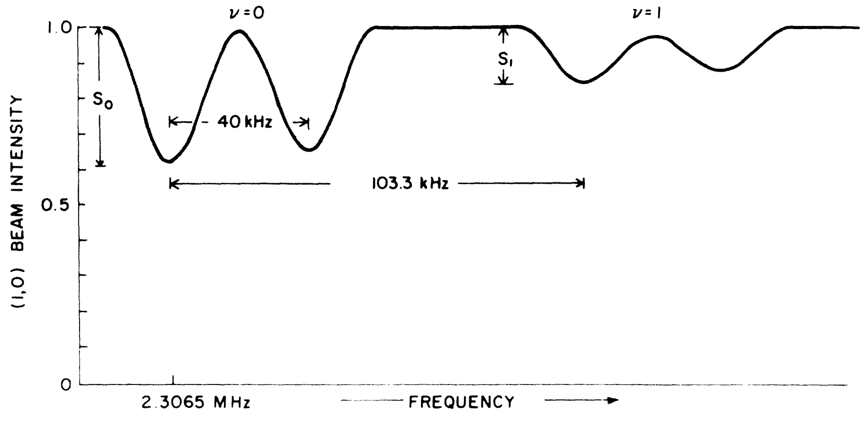

FIG. 4. Variation of the ^{6}LiF molecular-beam signal at the detector as a function of rf applied to a transition section. The C field strength is 262 V/cm.

pal part of a (1, 0) $v=0$ state and the molecule not be removed from the beam. This type of decay can occur only in the strong A and B fields and is sufficiently rare that the net effect on the measured lifetime is to reduce it by about 0.1%, a negligible amount.

In the field-free region between the oven and the A-field entrance, molecules in excited first vibration states may decay from pure (0, 0), (2, 0), and (2, ±1) states to (1, 0) $v=0$ states without any effect on the molecular trajectory. Thus the (1, 0) $v=0$ state grows between the oven and the A field, while the (1, 0) $v=1$ state both loses and gains population since it is also fed from the $v=2$ state. The combined effects of growth and decay upon the (1, 0) $v=0$ and $v=1$ states is to cause the relative populations of these states to depart from the relationship expressed in Eq. (4). Between the oven and the A field, the ratio of $v=1$ to $v=0$ states is given by $e^{-2l/3v\tau}$. This change is easily included merely by imagining the oven to A-field distance of 48 cm to be foreshortened by $\frac{1}{3}$, or by 16 cm. Thus we can continue to use Eq. (4), but our new effective apparatus length becomes 164 cm rather than 180 cm.

The final assumption considered is that the ratio S_1/S_0 correctly represents the ratio of vibration-state populations R. The question arises because both S_1 and S_0 can be controlled by the strength of the oscillatory electric field E_{rf}, as shown in Fig. 6. For a monovelocity beam, optimum (100%) transition probability occurs[12] when $\sin^2(2bl/v)=1$ or $2bl/v=\frac{1}{2}\pi$. Here l is the length of the oscillatory field while b is proportional to E_{rf}. We took care to find the optimal values of E_{rf} for all resonant signals (see Fig. 6). This is an important point, since the optimal value of E_{rf} clearly depends on beam velocity according to the criterion above that was verified by our experience. With a beam-velocity bandwidth of 5% and an E_{rf} which is nonuniform, about 70% of all available molecules were involved in a transition.

Thus there exists the possibility that as we systematically change the selected beam velocity, we systematically change the relative proportions of $v=1$ and $v=0$ molecules participating in their resonances. We believe that no such effect exists provided adherence is maintained to the following two experimental conditions: (i) use of the experimentally observed optimum values of E_{rf}; and (ii) use of Eq. (1) to compensate the A- and B-field voltages when changing selected beam velocity.

From Eq. (1) it can be seen that if the voltage-to-velocity ratio V/v is constant, the parameter p and thus the focusing properties of a quadrupole lens remain constant. This condition ensures that slower molecules follow the same paths through the apparatus as faster molecules, so all molecules should "see" the same geometric distribution of E_{rf}. The ratio V/v was held constant to 1 part in 4000.

To ensure that the above precautions eliminate systematic effects on the ratio S_1/S_0, we performed control measurements. First we tested the severity of condition (ii) by relaxing it to as much as

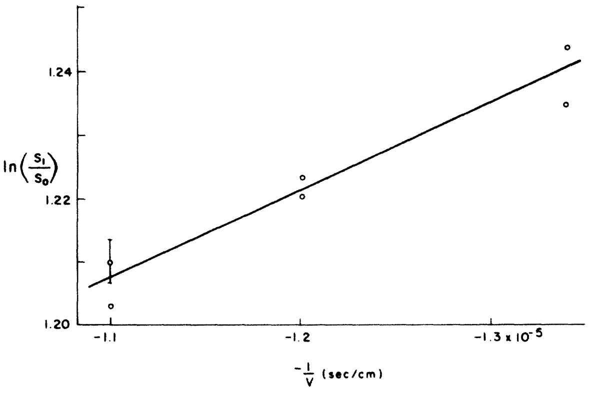

FIG. 5. Absolute values of the natural logarithm of the ratio S_1/S_0 of the $v=1$ to the $v=0$ signals at the detector as a function of negative recptrocal beam velocity.

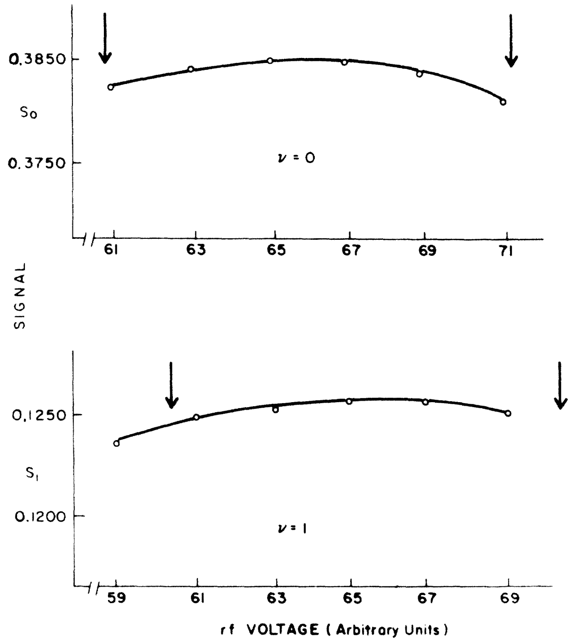

FIG. 6. Resonant signal strengths S_0, S_1 as a function of the rf voltage applied to a transition section for intermediate beam velocity. Arrows to the left and right indicate the shifts in the positions of maximum signals for 10% higher beam valocities, respectively.

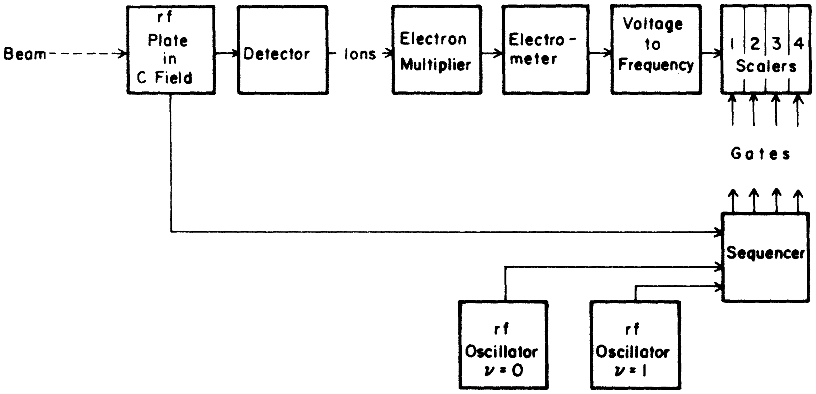

FIG. 7. Block diagram of the data acquisition system. The sequencer passes rf to the *C* field only when scalers 1 or 3 are gated on.

80 parts in 4000 with no apparent change in results. Next we compared values of S_1/S_0 obtained from two widely separated positions in the *C* field during the same run. Since the two transition regions cannot be expected to be identical, we obtained a measure of the sensitivity of S_1/S_0 to changes in radiofrequency field distribution. We even made physical changes only in position II and repeated the test. In none of these control measurements, numbering about 40, could we find any indication that S_1/S_0 was sensitive to the parameters being varied provided conditions (i) and (ii) were satisfied. Of the two conditions, (i) required the greater degree of compliance.

Thus we feel that changes in the ratio of S_1/S_0 that are observed as beam velocity is varied are effects of the finite lifetime of the $v=1$ vibration state, and that S_1/S_0 adequately represents R in Eq. (4).

Data taking was always preceded by a careful apparatus alignment culminating in use of the molecular beam as an indicator.

The data consisted of measurements of the relative signal strengths S_0 and S_1 resulting from (1, 0) to (1, ±1) transitions for $v=0$ and $v=1$ states, taken in a semiautomatic fashion as indicated in Fig. 7. Measurements of beam intensity with radiofrequency applied were sandwiched between full beam-intensity measurements and repeated cyclically in steps of about 2 sec. The gating and switching of radiofrequency were controlled by the sequencer shown in Fig. 7. Signal strengths were thus taken "simultaneously" and averaged over about 5 min.

The central resonant frequencies for all resonances were continually monitored, and we emphasize again that great care was taken to find the range of radiofrequency field strengths for which the induced resonances were maximized as shown in Fig. 6.

Because of velocity limitations imposed by our oven source, we were restricted to three beam velocities of about 8.0, 9.0, and 10.0×10^4 cm/sec.

RESULTS

The data from which we obtained the vibrational lifetime of the $v=1$ state of ^{6}LiF was collected in a series of ten runs. Table I gives the slopes of the absolute values of $\ln(S_1/S_0)$ when plotted against $-1/v$ for each run, together with an uncertainty which is the standard deviation for that run. The results for run 7 are shown in Fig. 5 where the points are of equal weight, as was the case for all runs, and the error bar represents the standard deviation for the set of data comprising a single point.

The average slope given in Table I is a weighted average, where each run was assigned a weight proportional to $1/\sigma^2$ according to usual procedures,[13] and the uncertainty is the probable error. The discrepancy from run to run is a consequence of the totality of error sources such as noise

TABLE I. Slopes obtained by plotting the absolute value of $\ln(S_1/S_0)$ as a function of negative reciprocal beam velocity. The standard deviation σ is shown for each run. Weighted average slope $\langle m\rangle = (11.5\pm1.8)\times10^3$ cm/sec.

Run	Slope m (cm/sec) ($\times10^{-3}$)	σ
1	10.8	1.1
2	17.6	1.0
3	12.7	5.0
4	13.0	2.7
5	16.1	2.7
6	8.5	1.5
7	13.7	0.7
8	15.7	1.5
9	10.5	0.3
10	10.3	1.5

bursts from the detector wire, random error in setting radiofrequency power and frequency, beam scattering from background gas, and varying hot wire detector efficiency. This latter factor was especially influential because it was necessary to compare data points taken as much as 45 min apart. Consequently, even small slow drifts in apparent beam strength can have large effects on the results of a particular run and constitute the major source of error. Such effects are random and tend to cancel when combining several runs. The average slope in Table I represents a change in the ratio S_1/S_0 of 90 ± 14 parts in 3300 for the slowest to fastest beam velocities. This change can be compared to the results of the 40 control measurements where the net change was 4 ± 6 parts in 3300.

Using the average slope of Table I and a measured length of 180 ± 10 cm or an effective length of 164 ± 10 cm, the lifetime corrected for effective length is

$$\tau = 14.3\,^{+2.7}_{-2.1}\ \text{msec},$$

where the uncertainty is the probable error.

In addition, we find the following relationship between $\mu^2 A$ in the first and ground vibration states:

$$(\mu^2 A)_1 = (1.0448 \pm 0.0002)(\mu^2 A)_0.$$

This latter result was obtained from the 103.3 ± 0.1 kHz separation of corresponding peaks in the $v = 1$ and $v = 0$ resonances when the $v = 0$ frequency was 2306.5 ± 0.1 kHz. It agrees well with previous measurements.[14,15]

DISCUSSION

The Einstein coefficient $A_{v,v-1}$ giving the decay rate from the v to the $v-1$ vibration state for (1, 0) molecules has the value[16]

$$A_{v,v-1} = \frac{64\pi f^3 v}{3hc^3} \,|\langle v|\mu|v-1\rangle|^2 \times \sum_{J'M'_J} |\langle(1,0)|\hat{r}|J',M'_J\rangle|^2, \tag{5}$$

where f is the frequency of the emitted infrared radiation, J' and M'_J are final rotation-state quantum numbers, $\hat{r}$ is a unit vector along the internuclear axis, and h and c are Planck's constant and the velocity of light, respectively. In the work reported here, $v = 1$. The terms in the summation over J' and M'_J are the fractional decay rates. The entire sum has the value unity and may be omitted when discussing the total decay rate. The electric dipole moment $\mu(r)$ for a diatomic molecule is given by the usual expansion about the equilibrium separation r_e,

$$\mu(r) = \mu_e + (r - r_e)\left.\frac{d\mu}{dr}\right|_{r=r_e} + \tfrac{1}{2}(r - r_e)^2 \left.\frac{d^2\mu}{dr^2}\right|_{r=r_e} + \cdots . \tag{6}$$

The only quantity in the expression for $A_{v,v-1}$ which cannot be measured from infrared spectroscopy data is the electric dipole matrix element. Since the first term of Eq. (6) contributes nothing to the matrix element, a measurement of the vibrational lifetime provides information about the remaining terms. Assuming that the vibrational states of a polar diatomic molecule may be represented by harmonic oscillator wave functions, only the odd-order derivative in Eq. (6) can connect vibration states whose quantum numbers differ by unity. Neglecting all terms beyond the second derivative and using appropriate conversion factors, the lifetime of the $v = 1$ state, $\tau_{1,0}$ (the inverse of $A_{1,0}$), may be written

$$\tau_{1,0} = \left(\frac{1.89 \times 10^5 m}{\omega^2}\right) \left|\frac{d\mu}{dr}\right|^{-2} \text{sec} . \tag{7}$$

In this expression m is the reduced molecular mass in atomic mass units, ω is the energy difference between vibration states in cm^{-1}, and $d\mu/dr$ is expressed in D/Å.

In order to compare the experimental lifetime with that predicted by Eq. (7), it is necessary to estimate the dipole moment derivative $d\mu/dr$. We turn first to the simple and often-quoted work of Rittner,[17] where the dipole moments of polar diatomic molecules are calculated classically as a sum of two terms, one from the separation r of two ionic cores and the other from the subsequent mutual polarization of each core by the other. The resulting expression for $\mu(r)$ depends on core polarizabilities, but $d\mu/dr$ can be expressed simply as

$$\frac{d\mu}{dr} = (3e - 2\mu/r), \tag{8}$$

which has the value 6.4 D/Å using the μ and r values of Wharten *et al.*[14] The corresponding value of $\tau_{1,0}$ is 22 msec.

Alternatively, we may approximate $d\mu/dr$ from existing spectroscopic data. We can simplistically estimate $d\mu/dr$ from the known vibrational dependence of μ as well as that of the rotational constant B, defined from the expression for the rotational energy $E_J = hBJ(J+1)$. Since B is proportional to r^{-2}, we can make use of the relationship $dB/B = -2\,dr/r$ to find dr. From the experimentally observed[14] changes in B and μ

as a function of vibration, we estimate $d\mu/dr$ in this manner to be 6.9 D/Å, or $\tau_{1,0} = 19$ msec. This value lies near the upper limit of our experimental result.

A somewhat more intricate method for obtaining estimates of $d\mu/dr$ from spectroscopic data begins with the expansion Eq. (6) and retains terms up to second order. After taking expectation values, $d\mu/dr$ can be written in terms of $r - r_e$, $(r - r_e)^2$ and $d^2\mu/dr^2$.[2] Since the known vibrational dependence of B involves expectation values of $r - r_e$ and $(r - r_e)^2$, the linear term can be obtained in terms of the quadratic which is then approximated by its harmonic oscillator value. The value of $d^2\mu/dr^2$ is estimated from Rittner's model and the resulting expression[18] for $d\mu/dr$ yields the value 4.9 D/Å and $\tau_{1,0} = 39$ msec. This result, far from the other estimates as well as our measured value, probably should not be taken seriously because of the estimates and approximations involved. In the case of KBr, for example, this latter method gives a large negative derivative while Rittner's simple picture predicts a smaller positive one much more in agreement with reality as inferred from the experimentally observed[2] dependence of μ on vibration.

The most significant comparison of our data with theory will be with values of $d\mu/dr$ calculated from reliable wave functions. Although such calculations are now feasible, none has yet been carried out.

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