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We have measured the Q branch vibrational Raman cross sections of the hydrogen halide gases HCl, HBr, and HI relative to that of N_2. We also measured the variation of the HI cross section as a function of the incident laser frequency. The absence of preresonance behavior in HI suggests that the virtual states primarily responsible for Raman scattering lie near or above the ionization potential. This in turn implies that the variation of the Raman cross section among the hydrogen halide molecules results primarily from a variation in the magnitude of the dipole matrix elements rather than from a variation in the energy of the virtual states involved.

INTRODUCTION

The values of the absolute vibrational Raman cross section of gas molecules are of interest for two reasons. First, these absolute cross sections are directly related to fundamental parameters describing the chemical bonds of the molecules. Second, knowledge of the relative total cross sections of various gases is essential for the use of Raman spectroscopy in the quantitative chemical analysis of gas mixtures.

In the last several years the absolute vibrational Raman cross sections for a number of common gases have been measured by laser techniques.[1-4] (Prelaser results have been tabulated in a convenient review.)[5] The recent measurements have generally been carried out by comparing the unknown cross section with that of the 2331 cm⁻¹ Q branch of N_2. The nitrogen Q branch cross section, although by itself not of fundamental scientific interest, is a very useful working standard. Hence, its absolute value has been measured by several groups using various techniques.[1-5]

Here we report measurements of the absolute Raman cross sections of the Q branches of the hydrogen halide gases HCl, HBr, and HI by a comparison with the nitrogen Q branch cross section. Since of these molecules HI has the lowest lying excited electronic states, we undertook to measure the frequency dependence of the HI cross section. Our observation are discussed in terms of the electronic spectra of these molecules, and in terms of two models which have been proposed for calculating Raman cross sections from other molecular parameters.

THEORETICAL BACKGROUND

The differential Raman scattering cross section per molecule $d\sigma/d\Omega$ can be defined by

$$I = (d\sigma/d\Omega) i_0 NV \ , \tag{1}$$

where i_0 is the incident irradiance (power per unit area),

I is the scattered radiant intensity (power per unit solid angle), N is the number of molecules per unit volume which are in the initial state of the Raman transition, and V is the experimental scattering volume. For a single freely rotating molecule and for an observation direction perpendicular to the polarization direction of linearly polarized incident light the differential Raman cross section for a transition from a state m to a state n is given by

$$\frac{d\sigma}{d\Omega} = \frac{16\pi^4}{9} \tilde{\nu}_s^4 \sum_{\rho\sigma} |(\alpha_{\rho\sigma})_{mn}|^2 \ . \tag{2}$$

Here $\tilde{\nu}_s$ is the frequency of the scattered light, $(\alpha_{\rho\sigma})_{kn}$ is the ρ, σth component of the polarizability derivative tensor evaluated between the initial (m) and final (n) molecular states. In the dipole approximation, these tensor elements can be written as

$$(\alpha_{\rho\sigma})_{mn} = \sum_e \prime \left[\frac{\langle m|R_\sigma|e\rangle \langle e|R_\rho|n\rangle}{E_e - E_m - E_0} + \frac{\langle m|R_\rho|e\rangle \langle e|R_\sigma|n\rangle}{E_e - E_n + E_0} \right]. \tag{3}$$

Here the summation is over all possible vibronic intermediate states e except for the initial and final states, the energy E_0 is that of the incident photon while E_m and E_n are those of the corresponding molecular states, and R_ρ and R_σ are many-electron dipole moment operators.

By applying the adiabatic approximation and the Herzberg–Teller expansion to (3), Albrecht[6,7] and collaborators have considered in detail the frequency dependence of $d\sigma/d\Omega$. Particular interest exists in ascertaining the behavior of the cross section in the frequecy regime where $d\sigma/d\Omega$ is not simply proportional to $\tilde{\nu}_s^4$, i.e., in the resonance or preresonance regime. They have shown that a diagonal component of this tensor $\alpha_{\rho\rho}$ can be written as the sum of two contributions.

The first of these dominates for the case in which a single electronic intermediate state makes the major contribution to the scattering activity. In this case the full frequency dependence of the Raman cross section

can be written in the dimensionless form

$$\frac{d\sigma}{d\Omega} \propto \left[\frac{\nu_s^2(\nu_e^2+\nu_0^2)}{(\nu_e^2-\nu_0^2)^2}\right]^2 , \qquad (4a)$$

where $\nu_e = E_e/h$ and $\nu_0 = E_0/h$. The second contribution dominates when most of the scattering activity arises from a Raman mechanism which includes two distinct but vibronically coupled virtual intermediate states.

In this mechanism a given electronic intermediate state e can be coupled vibronically with a whole set of other virtual states s_i. If the energies of these states are sufficiently high to permit the use of an average frequency ν_s, then the frequency dependency of the Raman cross section can be written as

$$\frac{d\sigma}{d\Omega} \propto \left|\frac{\nu^2(\nu_e\nu_s+\nu_0^2)}{(\nu_e^2-\nu_0^2)(\nu_s^2-\nu_0^2)}\right|^2 . \qquad (4b)$$

For both of these cases it is easily seen that deviations from a $d\sigma/d\Omega \propto \nu_s^4$ behavior become increasingly significant as the scattered photon energy approaches that of the electronic intermediate states.

Placzek[8] has simplified (2) by assuming that $E_e \gg E_0$ and $(E_e+E_m-E_n) \gg E_0$ and that both the incident and final states are in the ground electronic level. In this polarizability theory the intensity of molecular Raman scattering arises solely from the dependence of the ground state polarizability on nuclear motion. In this limit Eq. (2) can be written in the form

$$\frac{d\sigma}{d\Omega} = \frac{(2\pi)^4}{45} b^2 \bar{\nu}_s^4 g(45\alpha'^2 + 7\gamma'^2) . \qquad (5)$$

Here b is the zero point vibrational amplitude of the vibrational mode $[b = (h/8\pi^2 c\bar{\nu}_0)^{1/2}$, where $\bar{\nu}_0$ is here the zero-point vibrational frequency], g the degree of degeneracy, and $3\alpha'$ and γ'^2 are, respectively, the trace and anisotropy of the derivative of the polarizability tensor with respect to a normal coordinate and evaluated at the equilibrium position. The intensity of the Q branch $(\Delta J = 0)$ alone is given by Eq. (5) with γ'^2 replaced by $\chi\gamma'^2$. For linear molecules with moments of inertia greater than that of hydrogen, $\chi = 0.25$. For diatomic molecules, the molecular polarizability derivatives is related to the bond polarizability derivative, the derivative of the polarizability with respect to the nuclear separation, by

$$\alpha' = \frac{\partial\alpha}{\partial q} = \mu^{-1/2} \frac{\partial\alpha}{\partial r} , \qquad (6)$$

where α is the bond polarizability, r the internuclear distance, and μ the reduced mass.

EXPERIMENTAL PROCEDURE

The absolute Raman cross sections of the Q branch of HCl, HBr, and HI were measured relative to that of the Q branch of N_2 using the 488.0 nm line of the argon-ion laser as the exciting source. Raman scattering was observed in a direction perpendicular to both the direction of propagation and the direction of electric polarization of the incident laser beam. The scattered radiation was analyzed by a double monochromator and detected by a cooled S-20 photomultiplier connected to a dc elec-

trometer. The wavelength dependence of the sensitivity of the detection system was calibrated with a standard quartz–halogen tungsten lamp.

The gas samples were contained in a cubic stainless steel cell with fused quartz windows. The cell was connected to a stainless stell manifold which allowed the rapid interchange of the gases. For these absolute intensity measurements we used an external standard technique. The gas cell was filled with a single gas and then the Raman intensity measured. This procedure avoided the possible errors in measuring partial pressures which might arise as a result of incomplete mixing if the cell were to be filled with a mixture of gases (internal standard technique). The gas pressure in the cell, measured with a mercury manometer, was usually 1 atm.

The hydrogen halide gases were purified by freezing them in a liquid nitrogen cold trap and then pumping off the volatile impurities. The purity of the hydrogen halide gases was verified by the absence of any impurity bands in the Raman spectrum.

We measured the relative cross sections of the Q branches of HI and N_2 at each of six argon-ion laser wavelengths, 457.9, 476.5, 488.0, 496.5, 501.7, and 514.5 nm. For these frequency dependence measurements we employed an all glass gas handling system and an internal standard measuring technique. An internal standard technique was preferable for these relative frequency dependence measurements since here it was not necessary to know the exact concentration ratio in the gas sample. The measurements were repeated for a number of different mixtures. Since the Q branch Raman displacements for HI and N_2 differ by a small amount, little error was anticipated from uncertainties in the dispersion of the detection sensitivity.

In all of our intensity measurements we kept the spectrometer slits open wide enough so that the observed Raman line shapes were trapezoidal; hence, the absolute cross sections were simply proportional to the height of the trapezoids. Because of the large rotational constants of the hydrogen halides on the one hand, and because of the low depolarization ratio for N_2 on the other, the contribution of the 0 and S $(\Delta J = \pm 2)$ branches to the measured cross section was small compared to other experimental uncertainties.

RESULTS

In Table I we list our measured values for the total (polarized plus depolarized) Raman cross sections for the Q branches of HCl, HBr, and HI measured with 488.0 nm excitation. We have used our previously measured value of the total Raman cross section for N_2,[4] $d\sigma/d\Omega = (5.4 \pm 0.3) \times 10^{-31}$ cm^2/mol·sr. to obtain the cross sections for HCl, HBr, and HI. In this table we also list the cross sections computed from the mercury lamp data of Stansbury et al.[9] and a recent value for the HCl cross section reported by Schrotter.[10]

In addition, we list a value for the HF cross section obtained by LeDuff and Holzer[11] from a comparison of

TABLE I. Differential Raman cross section for the Q branch in hydrogen halide molecules for 488.0 nm excitation. The cross section for the 2331 cm^{-1} Q branch of N$_2$ is taken as $d\sigma/d\Omega = 5.4 \times 10^{-31}$ cm^2/mol·sr. All cross sections in units of 10^{-31} cm^2/mol·sr.

	ν (cm^{-1})	$\frac{d\sigma}{d\Omega}$ (HX)$\Big/\frac{d\sigma}{d\Omega}$ (N$_2$)	$\frac{d\sigma}{d\Omega}$ (HX)
HF	3962	0.91[a]	4.9[a]
HCl	2886	2.5±0.2,[b] 3.0[c]	14±1,[b] 10,[d] 16.2[c]
HBr	2558	4.2±0.4[b]	23±2,[b] 19[d]
HI	2230	6.0±0.6[b]	33±3[b]

[a]LeDuff and Holzer, Ref. 11.
[b]This work.
[c]Schrotter, Ref. 10.
[d]Stansbury et al., Ref. 9.

the magnitude of rotational and vibrational Raman scattering in HF. They calculated the HF rotational cross section from a measurement of the polarizability anisotropy by molecular beam electric resonance spectroscopy.[12]

We see that all values of the HCl and HBr cross sections are in reasonable agreement. Although we did not perform accurate depolarization ratio measurements, our rough values were in agreement with those reported by Perchard et al.[13]

In Fig. 1 we show the results of our measurements of the frequency dependence of the HI cross section. This plot was prepared in the following fashion. The measured ratios to the HI cross section to the N$_2$ cross section for each of the different incident wavelengths were divided by the respective values of the fourth power of the scattered frequency $\tilde{\nu}_s^4$. These numbers were then normalized by a constant factor so as to give a value of unity for 488.0 nm excitation and then plotted in Fig. 1 as a function of incident wavelength. The curves shown in Fig. 1 are calculated curves whose meaning is discussed below. The error bars in Fig. 1 are smaller than the corresponding ones in Table I because the data plotted in the figure are relative and not absolute measurements.

DISCUSSION

Detailed ultraviolet absorption studies have indicated a strong correspondence among the excited electronic states of HCl, HBr, and HI.[14,15] On this basis we can speculate that any conclusions we reach regarding the intermediate states involved in the Raman process for one of these molecules is valid for the whole group.

The uv absorption studies have shown that among the hydrogen halide gases the corresponding electronic levels decrease in energy with increasing molecular weight. To this fact Salant and Sandow[16] attributed their observation in 1931 of a relative increase in the Raman cross section in the order HCl, HBr, HI. They hypothesized that the decrease in the energy denominator of Eq. (3) for the heavier molecules accounted for the increase in Raman cross section.

The lowest lying electronic absorption in HI is from

the $^1\Sigma^+$ ground state X to a repulsive state with a $\sigma^2\pi^3\sigma^*$ configuration. This absorption is quite broad, beginning at ~27 500 cm^{-1} and peaking at ~48 000 cm^{-1}. Transitions to the lowest stable electronic excited states, a $^3\Pi$ state b and a $^1\Pi$ state c, both with $\sigma^2\pi^3\sigma$ configuration, are centered at ~56 740 cm^{-1} and ~62 320 cm^{-1}, respectively. Price[16] has also observed a series of Rydberg-like lines converging to the $^2\Pi_{1/2}$ state of the molecular ion HI$^+$ at 89 130 cm^{-1}.

The curves in Fig. 1 were calculated by substituting the various excited energy levels given above into Eq. (4a) for the frequency dependence of the Raman cross section. As with the experimental points, the cross sections have been divided by $\tilde{\nu}_s^4$ and the curves normalized to unity for 488.0 nm excitation. The labels of the curves correspond to the electronic transitions discussed above. We considered here only the first of the two mechanisms proposed by Albrecht, since frequency dependence curves obtained from Eq. (4b) would simply lie between the plotted curves.

All of the plotted curves predict that the Raman cross section for HI should vary faster with frequency than do our observed data. (We should emphasize that what we observed is really the frequency dependence of the HI Raman cross section relative to that for N$_2$. In our analysis we have assumed that there is no resonance enhancement of the N$_2$ Raman cross section in the frequency region under study. This assumption is consistent with our knowledge of the excited states of nitrogen as well as with our earlier measurements of the N$_2$ cross section.)[5] From Fig. 1 then, we draw the following conclusion: the important intermediate states for Raman
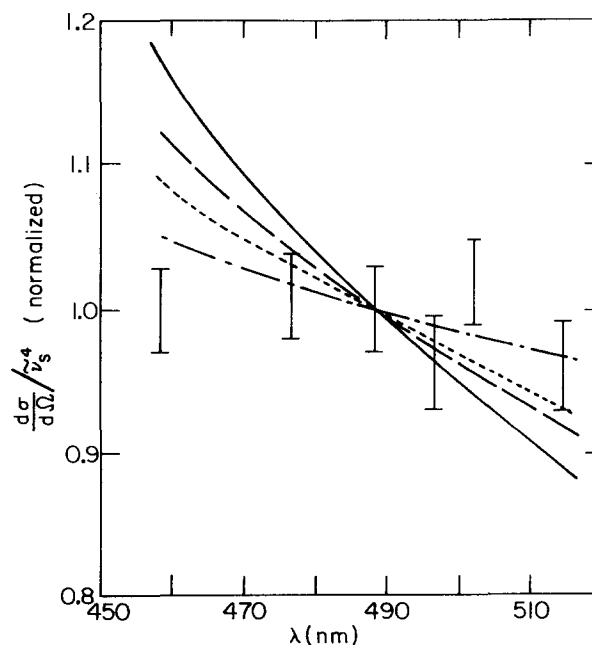

FIG. 1. HI Raman differential cross section divided by scattered frequency to the fourth power, $(d\sigma/d\Omega)/\tilde{\nu}_s^4$ vs incident wavelength λ. Cross section values normalized to unity for 488.0 nm excitation. Curves obtained from Eq. (4a): —, ν_e = 48 000 cm^{-1}; – – –, ν_e = 56 750 cm^{-1}; ···, ν_e = 62 320 cm^{-1}; —·—, ν_e = 89 130 cm^{-1}.

TABLE II. Values of Sellmeier resonance frequencies a and ionization potentials b for HCl, HBr, and HI. Frequencies in units of 10^4 cm^{-1}.

	ν_0 (cm^{-1})	I. P. (cm^{-1})
HCl	10.8853	10.4
HBr	9.8141	9.7
HI	8.532	8.91

[a]Reference 18.
[b]Reference 14.

scattering in HI lie near or above the first ionization potential. We suggest also that this conclusion is valid for the other hydrogen halides as well. In this connection we note that Schrotter[10] has recently reported that the frequency variation of the HCl Raman cross section shows no significant variation from ν_R^4 behavior for excitation as short as 364 nm. This result is completely consistent with our conclusion.

Further, our result is not dependent on the particular model of vibronic coupling which is chosen; calculations using the model of Peticolas et al.[17] yield a similar result. In addition, calculations which assume a single intermediate state and make us of the exact dispersion relation Eq. (3), also support our finding, although not quite so strongly since the explicit resonance denominator in this relation rises less steeply.

Measurements of the dispersion of the refractive indices of HCl, HBr, and HI are also consistent with our conclusion. The frequency dependence of the refractive indices n of these gases have been fitted to an expression of the Sellmeier form[18]

$$n - 1 = \frac{C}{\bar{\nu}_0^2 - \bar{\nu}^2} \quad , \qquad (7)$$

where $\bar{\nu}_0$ represents an average electronic resonance and C is a numerical proportionality factor. The values of $\bar{\nu}_0$ for HCl, HBr, and HI are given in Table II along with the ionization potentials suggested by Price[14] for these gases. For all three of the gases the two quantities are fairly close in value, and we can conclude that virtual transitions to states near the ionization potential make the major contribution to the refractive index as well as to Raman scattering. This correspondence is not unexpected.

A corrollary of the above result is that the variation in Raman cross section among the hydrogen halides does not arise primarily from the difference in the energy denominators. For, if we substitute the $^2\Pi_{1/2}$ ionization potentials of the hydrogen halide molecules as the intermediate electronic energy in an expression such as (4a), we get only a small cross-section variation among HCl,

TABLE III. Parameters for delta-function model from Pauling.[20]

	r (cm)	g	σ
HF	0.92×10^{-8}	1.72	0.499
HCl	1.28	1.62	0.786
HBr	1.42	1.59	0.875
HI	1.62	1.52	0.986

TABLE IV. Polarizability derivative $\partial\alpha/\partial r$ for hydrogen halide molecules in units of 10^{-16} cm^2.

	Experimental		Calculated	
	This work	Other	δfcn[a]	YB[b]
HF		0.99[c]	0.33	0.84
HCl	1.18 ± 0.06	0.98[d], 1.10[e]	1.29	0.97
HBr	1.40 ± 0.07	1.22[d]	1.90	1.00
HI	1.56 ± 0.08		3.03	1.09

[a]Long and Plane, Ref. 19.
[b]Yoshino and Bernstein, Ref. 21.
[c]LeDuff and Holzer, Ref. 11.
[d]Stansbury et al., Ref. 9.
[e]Schrotter, Ref. 10.

HBr, and HI. Hence, the important contribution to the variation in Raman cross section among these molecules probably arises from a variation in the size of the matrix elements.

Our data are insufficient to make any statement regarding the distinction between the two Raman mechanisms discussed earlier. An experimental determination of this distinction would require measurements taken in a frequency region where preresonance effects were, in fact, observed.

Since no preresonance behavior was observed, a discussion of the observed Raman cross sections in terms of polarizability derivations is appropriate. Two models which can be applied to diatomic hydride molecules have been proposed.

Long and Plane[19] have used a delta-function potential model in order to calculate $\partial\alpha/\partial r$ for A_1 symmetric stretching modes of diatomic and polyatomic molecules and ions. The essential feature of this model is that the nuclear Coulombic potential is replaced by a one-dimensional delta function. As a result of the one dimensionality of the model there is no contribution to $\partial\alpha/\partial r$ from the polarizability component perpendicular to the internuclear axis nor from the nonbonding electrons. The final expression for the bond polarizability derivative is

$$\frac{\partial\alpha}{\partial r} = \frac{2}{3}\frac{g\sigma}{Za_0}\frac{1}{2}nr^3. \qquad (8)$$

Here a_0 is the Bohr radius, r the equilibrium internuclear separation, $\frac{1}{2}n$ the bond number, σ the Pauling covalent bond character,[20] g the delta-function strength, and Z the effective nuclear charge is taken as the atomic number minus the number of inner-shell electrons. For heteronuclear diatomic systems they take $(g/Z)^{1/2}$ to be the geometric mean of the two atomic values. The values of the parameters of (8) for the hydrogen halides are given in Table III.

Yoshino and Bernstein[21] have proposed a semiempirical method for calculating the polarizability derivative for hydride molecules. They have assumed that the polarizabilities of all hydride molecules including hydrogen have the same functional dependence on the internuclear spacing and on the single atom polarizabilities. They determined the parameters for this function from their

measurements of the Raman cross section in hydrogen gas. The atomic polarizabilities required for the calculation were estimated by an empirical procedure.

In Table IV we list the values of $\partial\alpha/\partial r$ obtained from our cross-section measurements as well as other reported values for the polarizability derivatives of hydrogen halide molecules. We also list values for $\partial\alpha/\partial r$ predicted both by the delta-function potential model[19] and by the Yoshino–Berstein model.[21] We see that although the delta-function model does predict an increase of $\partial\alpha/\partial r$ with increasing molecular weight, the observed increase is much smaller than the predicted one. This breakdown of the delta-function model is not too surprising, since in this model heteronuclear molecules are treated as pseudohomonuclear ones; for HI this is not a good approximation. It appears then that the polarizability derivatives of the hydrogen halide molecules cannot be simply related to the degree of covalency of the molecules. We note that the delta-function model was used successfully in a study of the Raman intensities of the Group IV tetrahalides.[22]

The Yoshino–Bernstein model is seen to predict the proper order of magnitude for $\partial\alpha/\partial r$; it does not successfully predict the variation of $\partial\alpha/\partial r$ with molecular weight. The assumption of this model are probably much too crude to expect quantitatively accurate predictions for this system of molecules.

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