the observation zone. For a monolayer on the drop surface (10^{12} contributing molecules) the observed signal would imply an enhancement factor of the order of 10^6. This is perhaps somewhat larger than the enhancement factor estimated for the gas phase. The difference could be explained either by a multilayer SERS in the liquid, by less than a monolayer coverage of the drop surface in the gas phase experiment, or both.

The magnitude of the enhancement as well as the general character of our spectra show that SERS from liquid mercury surfaces is remarkably similar to that obtained by using roughened solid silver surfaces. A mercury surface is relatively smooth; experiment and theory indicate fluctuations only a few angstroms in amplitude.[11] Thus our results offer a congenial example for models that do not involve surface roughness.[12]

Acknowledgment. We gratefully acknowledge support of this work by a Chaim Weizmann Postdoctoral Fellowship (to O.C.) and by the Air Force Office of Scientific Research.

References and Notes

(1) For recent reviews, see (a) R. P. van Duyne in "Chemical and Biological Applications of Lasers", Vol. 4, C. B. Moore, Ed., Academic Press, New York, 1979; (b) E. Burstein, C. Y. Chen, S. Lundquist in "Light Scattering in Solids", J. L. Birman, H. Z. Cummins, and K. K. Rebane, Ed., Plenum, New York, 1979; T. E. Furtak and J. Reyes, *Surf. Sci.*, **93**, 351 (1980).
(2) J. E. Rowe, C. V. Shank, D. A. Zwemer, and C. A. Murray, *Phys. Rev. Lett.*, **44**, 1770 (1980); D. A. Weitz, T. J. Framila, A. Z. Genack, and J. I. Gersten, *ibid.*, **45**, 355 (1980).
(3) B. Pettinger, V. Wenning, and H. Wetzel, *Chem. Phys. Lett.*, **67**, 192 (1979); A. Girlando, M. R. Philpott, D. Heitmann, J. D. Swalen, and R. Santo, *J. Chem. Phys.*, **72**, 5187 (1980).
(4) F. W. King and G. G. Schatz, *Chem. Phys.*, **38**, 245 (1979); E. Burstein, Y. L. Chen, C. Y. Chen, S. Lundquist, and E. Tosatti, *Solid State Commun.*, **29**, 565 (1979).
(5) F. W. King, R. P. van Duyne, and G. C. Schatz, *J. Chem. Phys.*, **69**, 4472 (1978); S. Efrima and H. Metiu, *Chem. Phys. Lett.*, **60**, 59 (1978); *Isr. J. Chem.*, **18**, 17 (1979); *J. Chem. Phys.*, **70**, 1602, 1939, 2297 (1979).
(6) J. I. Gersten and A. Nitzan, *J. Chem. Phys.*, in press, and references cited therein.
(7) M. Moskovits, *J. Chem. Phys.*, **69**, 4159 (1978); J. I. Gersten, D. A. Weitz, T. J. Gramila, and A. Z. Genack, *Phys. Rev.*, in press.
(8) W. J. Choyke, S. H. Vosko, and T. W. O'Keefe, *Solid State Commun.*, **9**, 361 (1971).
(9) R. L. Birke, J. R. Lombardi, and J. I. Gersten, *Phys. Rev. Lett.*, **43**, 71 (1979).
(10) B. E. Conway and R. G. Barradas, *Electrochem. Acta*, **5**, 319 (1961).
(11) B. C. Lu and S. A. Rice, *J. Chem. Phys.*, **68**, 5558 (1978); J. S. Rowlinson, *Chem. Soc. Rev. (London)*, **7**, 329 (1978); M. Rao and B. J. Berne, *ACS Symp. Ser.*, **No. 86**, 72 (1978).
(12) Efrima and Metiu (ref 5) have shown that an image dipole model predicts strong SERS for mercury, comparable to silver. The validity of the image dipole mechanism has been questioned, however; see P. R. Hilton and D. W. Oxtoby, *J. Chem. Phys.*, **72**, 6346 (1980).

Pressure Broadening of Acetylene Rotational Raman Lines by Argon

M. Ceruti, D. Frenkel, and J. P. McTague*

Department of Chemistry, University of California, Los Angeles, California 90024 (Received: August 19, 1980)

The anisotropic interaction between acetylene and argon has been studied by observing the density dependence of the acetylene pure rotational Raman line broadening. The observed cross sections are approximately twice that predicted from the known polarizabilities and acetylene molecular quadrupole moment. An empirical atom–atom anisotropic potential adequately parametrizes the results.

Experiments on the pressure broadening of rotational Raman transitions provide information about the nature of the underlying intermolecular interactions, in particular about the anisotropic part of the intermolecular potential. For polar molecules, similar information can be obtained from the broadening of dipolar rotational transitions. In the case of nonpolar molecules, however, few spectroscopic techniques other than rotational Raman line broadening are sensitive to the anistropic part of the intermolecular potential. Despite this, very little experimental information is available on the rotational Raman line broadening of nonpolar molecules other than the simplest diatomics. In this note we report measurements on the width of the rotational Raman lines of acetylene (C_2H_2) broadened by argon. We compare our results with predictions based on the Fiutak–van Kranendonk[1] extension of Anderson's theory of pressure broadening.[2] Premixed samples of 99.6% pure, dust-free acetylene and argon were introduced into a variable temperature cell. The acetylene pressure was typically 1 atm, while the argon pressure ranged from 0 to 20 atm. The sample was illuminated by an argon ion laser ($\lambda = 514.5 \times 10^{-9}$ m). Rotational Raman scattering was studied in the conventional 90° scattering geometry.[3] Scattered light was analyzed by using a Spex double

monochromator, standard photon counting electronics, and a PDP 11/03 data acquisition system. Spectral resolution in most experiments was ~ 0.4 cm^{-1}. The instrumental function was determined by measuring the shape of the isotropic Rayleigh–Brillouin spectrum (the actual width of the Rayleigh–Brillouin triplet is completely negligible compared to the instrumental resolution). It was observed that the measured rotational Raman lines could be adequately represented as convolutions of the instrumental function and a Lorentzian.[4] The half-width of these best-fit Lorentzians was found to depend linearly on the argon density. Line-broadening cross sections were determined by using the relation

$$\sigma_{Ar-C_2H_2} = \langle v_{rel} \rangle^{-1} \frac{\partial \Delta \nu_{1/2}}{\partial \rho}$$

where $\langle v_{rel} \rangle = (8kT/\pi\mu)^{1/2}$. The slope $\partial \Delta \nu_{1/2}/\partial \rho$ was obtained by a linear least-squares fit. Cross sections for a number of rotational transitions of C_2H_2 have been collected in Table I. The intercept of the $\Delta \nu_{1/2}$ vs. ρ lines provides information about the C_2H_2 self-broadening. Our data were not sufficiently accurate to warrant further analysis of the C_2H_2 self-broadening.

TABLE I

$J \to J + 2$	$T = 295$ K			$T = 225$ K		
	σ_{EXP}/A^2	σ_{MULT}/A^2	σ_{LJ}/A^2	σ_{EXP}/A^2	σ_{MULT}/A^2	σ_{LJ}/A^2
$1 \to 3$	102	55	107	107	55	110
$2 \to 4$	106	53	102	99	52	104
$7 \to 9$	76	44	76	73	41	75
$8 \to 10$		42	74	82	38	73
$13 \to 15$	62	31	64	67	27	63
$14 \to 16$	78	29	62	65	26	60
$14 \to 21$	56	24	49	61	23	49
$20 \to 22$	45	24	47	71	23	46

TABLE II

	C_2H_2	Ar
α, A^3	3.49	1.64
$\alpha_\parallel - \alpha_\perp$, A^3	1.86	0
U, eV	11.4	15.76
Q, esu cm$_2$	3×10^{-26}	0
ϵ_{LJ}, K	185	119.8
σ_{LJ}, A	4.221	3.405
$\epsilon_{C_2H_2-Ar}$, K	148.9	
$\sigma_{C_2H_2-Ar}$, A	3.81	
d_{EFF}, A	1.86	

The intermolecular interaction between an atom and a linear molecule can be written in the following form:

$$V(\vec{r},\vec{u}) = \sum_{l=c}^{\infty} v_l(r) P_l(\vec{1}_r \cdot \vec{u}) \tag{1}$$

where $\vec{u}$ is a unit vector along the molecular axis. For molecules with inversion symmetry only even l contribute. For not too small r, $v_l(r)$ can be expanded as

$$v_l(r) = \sum_{n=n_{min}}^{\infty} C_{l;n} r^{-n} \tag{2}$$

Explicit expressions for the leading $C_{l;n}$ may be worked out if the molecular multipoles and polarizabilities are known.[5] In particular, for an atom–linear (nonpolar) molecule system:

$$C_{2;6} = -\tfrac{1}{2} U_a U_2/(U_1 + U_2)\alpha_2(\alpha_\parallel - \alpha_\perp)$$

$$C_{2;8} = -\tfrac{1}{27}\alpha_2 Q_1^2$$

$$C_{4;8} = -\tfrac{9}{7}\alpha_2 Q_1^2$$

Values for the ionization potentials (U), the molecular polarizability components ($\alpha_\parallel$, $\alpha_\perp$), and the molecular quadrupole moment for the C_2H_2–Ar system are collected in Table II.

Once the intermolecular potential is specified, rotational line broadening cross sections may be calculated by using an appropriate model. We evaluated the C_2H_2–Ar line broadening cross sections in the straight-trajectory approximation.[1,2] The results of these calculations are shown in Table I. Clearly, the leading terms in the multipole series are not sufficient to explain the observed line broadening.

An approximate C_2H_2–Ar potential that is compatible with the line broadening data was constructed in the following way. It was assumed that the C_2H_2–Ar system behaves effectively as an atom–diatom system, with atom–atom Lennard-Jones interactions. The ϵ's and σ's for this atom–atom interaction were estimated from the potential data of ref 6 and the Lorentz–Berthelot combination rules. The values are given in Table II. In terms of ϵ, σ, and d (the effective "atom–atom" separation in C_2H_2), the leading anisotropic term in the C_2H_2–Ar potential is of the form

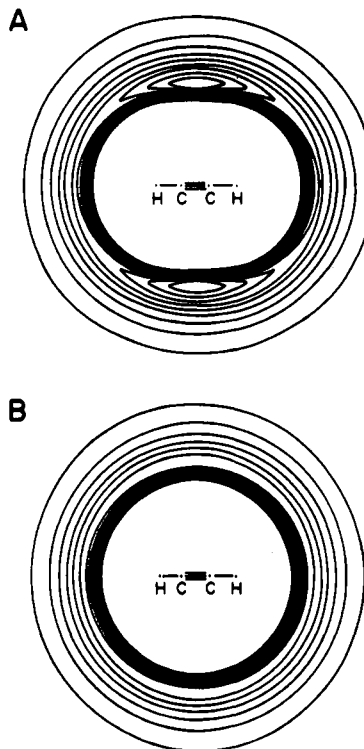$$v_2(r,\vec{u}) = -8d^2(4\epsilon\sigma^6)P_2(\vec{1}_r \cdot \vec{u})r^{-8} \tag{4}$$

Figure 1. Contour plots of the C_2H_2–Ar potential surface (A) assuming atom–atom Lennard-Jones interaction with the parameters as given in Table II; (B) using the same isotropic potential as in (A), but with anisotropic contributions as given by eq 3 and the multipole moments in Table II. The resolution of the contour lines is 15 K.

d was considered an adjustable parameter. Using the above potential in a straight-trajectory calculation we obtained a satisfactory fit of the experimental line broadening data for $d = 1.86$ Å (see Table I). The C–C distance in C_2H_2 is 1.20 Å while the H–H distance is 3.32 Å. The present value for the separation between the effective centers of interactions therefore appears reasonable. Over the range of distances relevant for line broadening, this empirical potential surface is considerably more anisotropic than the multipole expansion would suggest, as can be seen from Figure 1.

References and Notes

(1) J. Flutak and J. van Kranendonk, *Can. J. Phys.*, **40**, 1085 (1962).
(2) P. W. Anderson, *Phys. Rev.*, **76**, 647 (1949).
(3) B. J. Berne and R. Pecora, "Dynamic Light Scattering", Wiley, New York, 1976.
(4) The contributions of vibrationally excited molecules to the rotational Raman lines were neglected.
(5) A. D. Buckingham, *Adv. Chem. Phys.*, **12**, 107 (1967).
(6) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1954.