Collision Induced Raman Scattering as a Probe of Covalent Bonding in Mercury Diatoms

Simone Ceccherini and Massimo Moraldi
Istituto Nazionale di Fisica della Materia, Unità di Ricerca di Firenze, Firenze, Italy
and Dipartimento di Fisica, Università di Firenze, Largo E. Fermi 2, I-50125 Firenze, Italy
(Received 8 May 2000)

We show that collision induced Raman spectra of mercury vapors can be understood if a specific contribution to the pair polarizability due to covalent contribution to interatomic interaction is taken into account. Such a result is important because it demonstrates the possibility to use Raman spectroscopy in order to study the nature of the short range interaction in mercury and presumably in all divalent metal pairs.

PACS numbers: 31.70.–f, 33.20.Fb, 34.20.Cf

Mercury has been studied with great care in the past years. Spectroscopic measurements of mercury dimers are available from which it has been possible to extract information on the interatomic potential [1–4]. Also *ab initio* calculations of the interatomic potential have been communicated where, in particular, it has been pointed out that an important covalent contribution to bonding should be present [5,6]. In another series of papers the arising of a covalent bonding has been studied as a function of cluster dimension both experimentally [7–11] and theoretically [12–16]. It is now rather well established that when increasing the size of the cluster of mercury atoms there is a transition from van der Waals to covalent and metallic bonding. It is thus important to understand the role of the covalent bonding in the mercury-mercury interaction in order to get a better insight into the transition to the metallic phase.

A few years ago a paper [6] appeared with the calculation of the average of the squared deviation of the charge $e^2\langle\delta N^2\rangle$ on a mercury atom in the presence of a second one at a distance R (e is electron charge). Such a deviation indicates the presence of ionic configurations in the ground electronic state of a pair of mercury atoms. The charge fluctuation amounts to about 0.2 (in atomic units) at the distance R_m (where the potential is minimum). Just as a comparison with a van der Waals pair it was noted that the same fluctuation for helium amounts to 0.01. It is finally worth noting that ionic configurations admit exchange of electrons and thus the formation of covalent bonding.

In this Letter we want to discuss some recent results [17] of collision induced (CI) Raman scattering on low density mercury vapors and show that they can be accounted for once the contribution of the ionic configurations on the CI polarizability is taken into account. In this way we demonstrate for the first time that CI Raman scattering is an appropriate technique to show the existence of covalent bonding in pairs of mercury atoms.

In order to show that we will take advantage of the great quantity of data relative to pure van der Waals pairs like rare gas atoms. CI spectra of low density rare gas atoms have been studied both experimentally and theoretically (see references cited in [18]). It is now established with reasonable accuracy that pair polarizabilities of such complexes are explained by means of induction mechanisms that originate from electrostatic and exchange interactions. Electrostatic induction mechanisms are rather well known, at least at large interatomic distances. Exchange effects are less well known but it is always recognized that they give a negative contribution to the pair polarizability. Such effects, both electrostatic and, even though to a lesser degree, the exchange ones, scale with the atomic polarizability while distances are to be rescaled by its cubic root [18]. However, the application of this model to mercury indicates that, in order to reproduce the Raman spectrum, it is necessary to introduce, in the previous model, a large positive contribution to the pair polarizability [19–21,17,22]. We will show that such a contribution can be justified with the existence of sizable charge fluctuations in the electronic ground state of the atomic pair.

We now want to derive an approximate expression for the contribution to the pair polarizability due to the mixing of ionic configurations in the ground state. We will assume for simplicity that only two valence electrons for each atom take part in the determination of the interaction. Such an assumption is not relevant to the general aspects of the result that we will arrive at, though.

The ground electronic state of the two atoms can be written, when neglecting the interaction of the atoms, as

$$\Psi_g^{[0]} \sim |s_A\chi_{1/2}s_A\chi_{-1/2}s_B\chi_{1/2}s_B\chi_{-1/2}|, \qquad (1)$$

where A and B indicate the positions of the two nuclei, s_A and s_B are atomic orbitals of s type relative to nuclei A and B, respectively, and χ_μ is the spin eigenfunction with projection μ on the quantization axis. Finally $|\cdots|$ indicates a Slater determinant.

When the interatomic interaction is taken into account, the ground state mixes with excited configurations of the pair. Such excited states are both purely atomic and ionic. Moreover, because we are interested in understanding the role of ionic configurations in the induced polarizability, we will retain only the mixing with ionic configurations. Thus, the ground state Ψ_g has a form like

$$\Psi_g = \Psi_g^{[0]} + \lambda\psi_{\text{ion}}\,, \tag{2}$$

where λ indicates the amount of ionic configurations (ψ_{ion}) in the ground electronic state. It is such an amount that determines the charge fluctuations on each atom and thus such fluctuations will be related to λ in a way that will be determined in the following. We can think that ionic configurations are such that one single valence s electron is on one atom and two s electrons plus a p electron are on the other atom [13]. We thus get a degeneracy related to the cases for which the negative ion is formed either on atom A or on atom B. An ionic configuration with a definite value of the total spin S, M_S can be written as

$$\psi_A^{(i)}(S,M_S) \sim \sum_{\mu,s,m} C(1/2,1/2,\mu_1,\mu_2;s_1,m_1) \times C(1/2,1/2,\mu_3,\mu_4;s_2,m_2)C(s_1,s_2,m_1,m_2;S,M_s)\,|s_A\chi_{\mu_1}s_A\chi_{\mu_2}p_A^{(i)}\chi_{\mu_3}s_B\chi_{\mu_4}|\,, \tag{3}$$

which represents a configuration in which atom A is negative and atom B is positive. $C(\cdots)$ are Clebsh-Gordan coefficients and the superscript i indicates the direction ($i = x, y, z$) of the p orbital.

Neglecting interatomic interactions that depend on spin, only $S = 0$ configurations can mix to $\Psi_g^{[0]}$. In the following it will be understood that ψ_{ion} represents only $S = 0$ states. In this case we can form the two combinations

$$\Psi_\pm^{(i)} = \frac{1}{\sqrt{2}}[\psi_A^{(i)} \mp \psi_B^{(i)}], \tag{4}$$

which are symmetric (Ψ_+) and antisymmetric (Ψ_-) for inversion of electron positions. Moreover, $\Psi_+^{(i)}$ will give rise to bonding whereas $\Psi_-^{(i)}$ to antibonding. The atomic orbital p can be directed along the internuclear axis (z axis) or orthogonally to it (x, y axes). The strength of the bonding (antibonding) will be determined by the superposition integral of, say, orbital $p_A^{(i)}$ with orbital s_B, that we name Q_i. It is to be expected that most bonding will be obtained with $i = z$ (maximum superposition) and thus ψ_{ion} in Eq. (2) is to be replaced by $\Psi_+^{(z)}$.

In the presence of an electric field, the ground state wave function (which is symmetric for position inversion) will mix with antisymmetric states

$$\Psi_g(E_i) = \Psi_g + \frac{\langle\Psi_-^{(i)}|D_iE_i|\Psi_g\rangle}{\Delta_i}\Psi_-^{(i)}\,, \tag{5}$$

where Δ_i is the energy of the antisymmetric state $\Psi_-^{(i)}$ minus the ground state energy. D_i is the ith component of the electric dipole moment of the pair of atoms.

Because a negative mercury ion is unstable we can assume that the energy difference of the ionic states with respect to the ground state is about I_p (atomic ionization potential) plus the electrostatic energy $-e^2/R$ where R is the internuclear distance. We will thus replace in the previous equation Δ_i with $I_p - e^2/R$.

The components of the polarizability can be calculated by using Eq. (5),

$$\alpha_{ii} = 2\left\langle \frac{d\Psi_g(E_i)}{dE_i}\right|_{E=0} |D_i|\Psi_g\rangle = \frac{2}{I_p - e^2/R}\,|\langle\Psi_-^{(i)}|D_i|\Psi_g^{[0]}\rangle + \lambda\langle\Psi_-^{(i)}|D_i|\Psi_+^{(z)}\rangle|^2. \tag{6}$$

The matrix elements appearing in the previous equation can be evaluated as expansions of powers of superposition integrals Q_i (superposition integrals of s atomic orbitals on different atoms will be neglected). By retaining the first significant contribution we get

$$\begin{aligned} \langle\Psi_-^{(i)}|D_i|\Psi_g^{[0]}\rangle &\sim \delta_{i,z}\frac{eRQ_i}{\sqrt{2}}\,, \\ \langle\Psi_-^{(i)}|D_i|\Psi_+^{(z)}\rangle &\sim \delta_{i,z}eR\,, \end{aligned} \tag{7}$$

where $\delta_{i,z}$ is the Kronecker symbol. It is seen that $\alpha_{xx} = \alpha_{yy} = 0$. Such a result is a consequence of our model for which the dipole induced by the electric field is originated only by a transfer of charge from one atom to the other. We will thus name β_{cf} ($= \alpha_{zz} - \alpha_{xx}$) such a contribution to the polarizability anisotropy

$$\beta_{\text{cf}} = \frac{e^2}{I_p - e^2/R}2\lambda^2\left(1 + \frac{Q_z}{\sqrt{2}\lambda}\right)^2 R^2\,. \tag{8}$$

As said previously, λ^2 can be related to $\langle\delta N^2\rangle$. The squared modulus of the ground state wave function is composed of three terms [see Eq. (2)]:

$$\begin{aligned} |\Psi_g|^2 = |\Psi_g^{[0]}|^2 \times (1 - \lambda^2 - 2\sqrt{2}\,\lambda Q_z) + \lambda^2|\Psi_+^{(z)}|^2 \\ + 2\lambda\Psi_g^{[0]}\Psi_+^{(z)}\,. \end{aligned} \tag{9}$$

To the first term we can associate a null net charge on each atom and to the second term a charge $\pm e$. As far as the third term is concerned, which results both from atomic and ionic contributions, we assume that it contributes with a charge fluctuation $\pm e/2$. The squared charge fluctuation is thus equal to

$$\langle\delta N^2\rangle = \lambda^2 + \lambda Q_z/\sqrt{2}\,, \tag{10}$$

and thus

$$\beta_{\text{cf}} = \frac{e^2}{I_p - e^2/R}2\langle\delta N^2\rangle\left(1 + \frac{Q_z}{\sqrt{2}\lambda}\right)R^2. \tag{11}$$

At this point a relation is needed between Q_z and λ. In order to do that we minimize with respect to λ the quantity $\langle\Psi_g|H|\Psi_g\rangle$ where Ψ_g is given by Eq. (2). A simplified model obtained by two electrons shows that at relatively large interatomic distances we have

$$\lambda \sim \frac{X/\sqrt{2}}{-I_p + e^2/R} \qquad (12)$$

with X a resonance integral,

$$X = \sqrt{2}\langle \Psi_g^{[0]} | V | \Psi_+^{(z)} \rangle \sim -\frac{2e^2}{R} Q_z\,, \qquad (13)$$

where, in the second equality, we have assumed the resonance integral X to be proportional to the superposition integral Q_z with a proportionality coefficient given by $-2e^2/R$. Such an assumption is rather crude; more refined models would be needed for more quantitative results which, however, will not be considered here. With such an assumption we get

$$\lambda \sim \frac{\sqrt{2}\,e^2}{R} \frac{Q_z}{I_p - e^2/R}\,, \qquad (14)$$

and finally

$$\beta_{\rm cf} \sim \langle \delta N^2 \rangle R^3 \left(1 + \frac{2e^2/R}{I_p - e^2/R}\right). \qquad (15)$$

The expression for the polarizability in Eq. (15) represents the contribution that arises from the fluctuations of charge on each single atom. Such a fluctuation is relatively small for helium. It is thus to be expected that such a contribution is practically absent in helium (and in all rare gas systems), but it may become significant in mercury (and even more important in other liquid metal vapors). Here we will assume for the total polarizability β in mercury an expression that contains both the rare gas ($\beta_{\rm rg}$) and the charge fluctuation ($\beta_{\rm cf}$) contributions

$$\beta = \beta_{\rm rg} + \beta_{\rm cf}\,, \qquad (16)$$

where $\beta_{\rm rg}$ is obtained from Eq. (12) in [18] with α_0 the mercury atomic polarizability (38.5 a.u.) and r_1 (= 1.25 a.u.) extrapolated from the rare gas values. Such an extrapolation is rather arbitrary but it hardly affects our final results because $\beta_{\rm rg}$ at short interatomic distances, where the exchange contribution is important, is almost negligible with respect to $\beta_{\rm cf}$ (see Fig. 1).

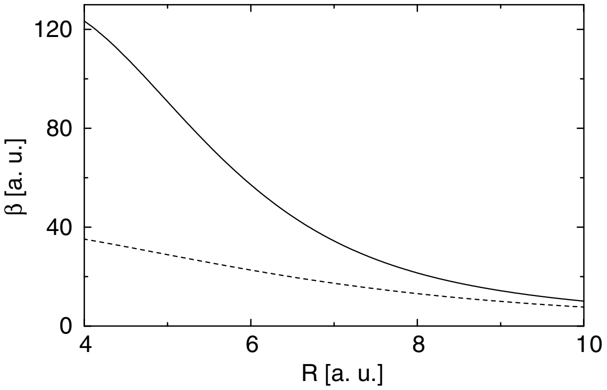

FIG. 1. Solid line: total polarizability anisotropy. Dashed line: rare gas contribution ($\beta_{\rm rg}$) to the polarizability anisotropy.

In order to get $\beta_{\rm cf}$ from Eq. (15) we need, apart from $I_p = 10.44$ eV, the function $\langle \delta N^2 \rangle$. Here we use the CI Raman spectra [17] to determine it. The Raman spectra can be numerically evaluated according to standard procedures and by means of a computer code [23]. An interatomic potential for mercury is needed: we have used the one derived in [22] that is able to reproduce both dimeric energies and low density viscosity data. We find that the measured Raman spectrum can be reproduced with a $\langle \delta N^2 \rangle^{1/2}$ that is shown in Fig. 2 as a solid line. In the same figure, as a dashed line, the estimation of the same quantity in [6].

The measured Raman spectrum and the one calculated by means of Eq. (16) are reported in Fig. 3. In the same figure also the spectrum calculated by neglecting $\beta_{\rm cf}$ is reported (dashed line): the comparison with the measured spectrum shows the inadequacy of the rare-gas model for mercury.

The comparison of $\langle \delta N^2 \rangle^{1/2}$ calculated in Ref. [6] with the one derived here (Fig. 2) shows that our model for $\beta_{\rm cf}$ is quite reasonable. Discrepancies are relatively larger as the interatomic distance increases. Indeed, as interatomic distance increases, the $\beta_{\rm cf}$ contribution becomes relatively smaller (see Fig. 1) and, consequently, its determination is less reliable. On the other hand, in the range of distances that mostly affect the Raman spectrum (6–7 a.u.), the relative deviation of $\langle \delta N^2 \rangle^{1/2}$ as derived here with the one calculated in [6] amounts to about 25%, which we think is quite acceptable in view of all the approximations used in the present work.

As a consequence, we have demonstrated the role of charge fluctuations in the polarizability anisotropy of mercury pairs and have indicated a method to estimate it by means of CI Raman spectra. The same method is clearly applicable to all systems in which charge fluctuations are relevant (the first candidates being the other metal vapors like Cd and Zn).

We thank Professor L. Frommhold for providing us with the computer code for the calculation of the Raman

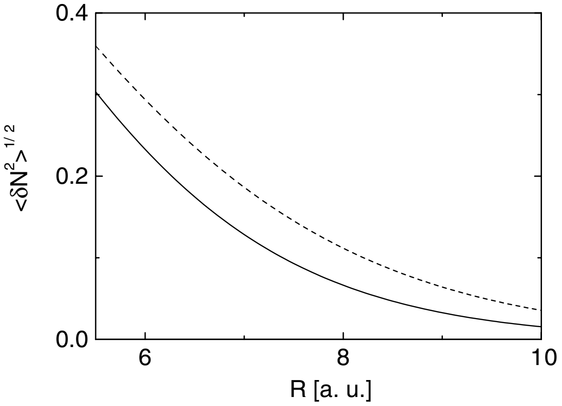

FIG. 2. Solid line: charge fluctuation $\langle \delta N^2 \rangle^{1/2}$ (in a.u.) derived from Raman spectrum. Dashed line: $\langle \delta N^2 \rangle^{1/2}$ evaluated in [6].

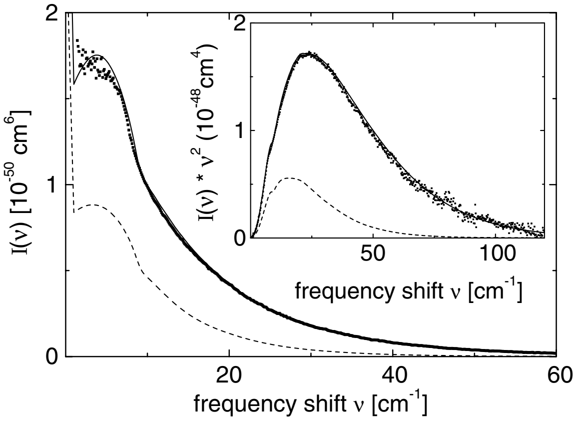

FIG. 3. Squares: measured Raman spectrum [17]. Solid line: Raman spectrum calculated with β_{cf} contribution. Dashed line: Raman spectrum calculated without β_{cf} contribution. In the inset same as before for Raman intensity multiplied by frequency shift squared.

spectrum, and Professor F. Hensel for pointing out to us the importance of charge fluctuations in the determination of the pair polarizability.

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