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ENERGY DISSIPATION BY A LONGITUDINAL RAMAN PROCESS*

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Abstract

The concept of a longitudinal Raman process is introduced to encompass the indirect transmission of energy from slow electrons to nuclei through the reversible polarization of surrounding electrons. Experimental approaches are sought to assess this process quantitatively.

Introduction

We consider the energy dissipation from subexcitation electrons,¹ viz., those electrons with kinetic energies too low (of the order of eV) to excite electronic levels in a material. These electrons are abundantly produced in materials under the action of any ionizing radiation; indeed, their total number equals the total number of ions produced. These electrons are important as precursors of various species produced by radiation.^{1,2} In the present letter we offer a general approach for treating, on equal footing, the energy dissipation of subexcitation electrons in both gases and condensed matter. (The notion of subexcitation electrons is useful for insulators and semiconductors, but not for metals, in which conduction electrons are excited even by thermal agitation.)

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Because the de Broglie wavelength of a subexcitation electron is on the order of a nanometer (nm), a typical value of the momentum transfer in an inelastic process is on the order of $\hbar/\text{nm}$ or less. This means that the excitation of nuclear motion by any direct interaction is improbable in general, because it requires a much greater momentum transfer, amounting to hundreds of $\hbar/\text{nm}$, owing to large nuclear masses. In addition, the Coulomb interaction makes the direct excitation of nuclear motion especially improbable because of its long range; recall that the Fourier component of the Coulomb interaction for momentum transfer $\hbar q$ is proportional to $1/q^2$ and is therefore dominant at low q . Evidence for the low probability of rotational and vibrational excitation due to direct Coulomb interaction is extensive for gaseous molecules.³

In this respect, resonances and other indirect mechanisms constitute an exception and are effective in transferring appreciable momentum to nuclear motions. A subexcitation electron having the right energy and angular momentum can then become trapped by a molecule at least temporarily, causing a substantial change in the internuclear forces, which is often discussed in terms of adiabatic potentials. The role of resonances in vibrational excitation in gaseous molecules has been well known since the pioneering work of Schulz,⁴ as fully documented later.^{2,3,5}

The role of resonances in molecular solids has been studied by Sanche and co-workers.⁶ Among the wealth of their experimental findings, it is particularly notable that in molecular solids a resonance always seems to lead to some energy loss rather than to elastic scattering, whereas in gases a resonance commonly results in either elastic or inelastic scattering.⁴ Fano, Stephens, and Inokuti⁷ interpreted the dominance of the inelastic scattering as being attributable to polarization hysteresis. That is, once an electron enters a resonance state and is thus localized even temporarily, the nearby molecules in the medium experience electrostatic polarization that fails to relax completely during the eventual escape of the electron. The subsequent work of Stephens and Fano⁸ implied that the electron loses energy mainly in the form of many long-wavelength phonons, but no quantitative estimates were made. Fano and Du⁹ further discussed electron resonance trapping in a molecular crystal. Recently, Mills¹⁰ formulated the idea into a theory leading to quantitative results.

Nevertheless, whether the lifetime of a resonance state is sufficiently long to cause substantial polarization remained unclear.

We now enlarge upon the notion of Refs. 2 and 3 that the interactions of an electron with molecules of the medium can affect nuclei through a secondary effect of elastic polarization, stressing that this effect amounts to a generic *longitudinal Raman process*, whether in gas molecules or condensed matter. Recall that the familiar Raman process induced by a photon in the visible spectrum occurs through virtual electronic excitation with negligible momentum transfer, which nevertheless imparts energy to nuclear motion, usually in vibrational excitations. In the familiar Raman process, the virtual excitation is transverse to the light propagation. The process we envisage in contrast is induced by longitudinal Coulomb interactions, leading initially to the *elastic* (meaning reversible) polarization of molecules and thence to nuclear excitations. These Coulomb interactions include a wealth of short-range components whose relevance failed to emerge in the approach of Stephens and Fano.⁸

This view of energy dissipation by slow electrons adds a new element to Bohr's early analysis¹¹ of dissipation by *fast* charged particles. Collisions by fast charges are "impulsive," meaning that their energy loss equals the sum of the recoil energies of single electrons or nuclei, *regardless* of correlations among these constituents of matter. In contrast, such correlations become essential in our context of incident electrons slower than the electrons of the matter yet faster than nuclei. The occurrence of two different time scales causes electrons of the to recoil *elastically* except insofar as they react on nuclei.

To state our idea more quantitatively, we begin with the Born-Oppenheimer approximation, considering the electronic polarizability of an aggregate of atoms and molecules at fixed positions $\vec{R}_\lambda$ of all nuclei λ , in the dipole limit (i.e., at the limit of small momentum transfer) for the time being. The polarizability $\alpha(\omega; \vec{R}_1, \vec{R}_2, \dots)$ at frequency ω (i.e., corresponding to energy transfer $\hbar\omega$) depends parametrically on $\vec{R}_\lambda$. According to the Hellmann-Feynman theorem,¹² the derivative $\partial\alpha(\omega; \vec{R}_1, \vec{R}_2, \dots)/\partial\vec{R}_\lambda$ determines the force acting on the nucleus λ ; note that the electronic polarization means a distortion of the electron cloud and hence of chemical bonds within a molecule or in a larger aggregate of neighboring

atoms. The distortion can readily transfer appreciable momentum to nuclei, even though most of the momentum may be returned to the electron upon its departure; still, a small part of the momentum accompanies the net inelasticity.

Recall the definition of the dipole polarizability: the Fourier component $\vec{E}(\omega)$ at frequency ω of a spatially uniform electric field induces a dipole moment

$$\vec{d}(\omega) = \alpha(\omega) \vec{E}(\omega). \quad (1)$$

Here $\alpha(\omega)$ represents the thermal average of $\alpha(\omega, \vec{R}_1, \vec{R}_2, \dots)$ over $\vec{R}_\lambda$. The electric field induces the electric polarization $\vec{P}(\omega)$ of a macroscopic material, given by

$$\vec{P}(\omega) = \chi(\omega) \vec{E}(\omega), \quad (2)$$

where $\chi(\omega)$ is the dielectric susceptibility. For a material at vanishingly low density N , $\chi(\omega)$ simply equals $4\pi N\alpha(\omega)$ in the cgs system. However, the relation between $\chi(\omega)$ and $\alpha(\omega)$ is in general more complicated because of the local field, a subject of extensive treatments since the pioneering work by Clausius and Mosotti. Schnatterly and Tarrio¹³ recently published an excellent review on this topic, including a discussion of the local-field's dependence on the momentum transfer $\hbar q$.

Evaluation of the Probability for a Longitudinal Raman Process

Consider an incident electron at position $\vec{r}$. A condensed medium consists of electrons at positions $\vec{r}_j$ and of nuclei of charge $Z_\lambda e$ at positions $\vec{R}_\lambda$, with the unperturbed Hamiltonian H_m . The Coulomb interaction V between the incident electron and the medium

$$V(\vec{r}, \vec{r}_j, \vec{R}_j) = (e^2 / 2\pi^2) \int d\vec{q} q^{-2} e^{-i\vec{q} \cdot \vec{r}} \left[\sum_j e^{i\vec{q} \cdot \vec{r}_j} - \sum_\lambda Z_\lambda e^{i\vec{q} \cdot \vec{R}_\lambda} \right], \quad (3)$$

will be treated as perturbation. In the initial state li with total energy E_i , the electron has momentum $\hbar \vec{k}_i$, the medium electrons are in the ground state 0_e , and the nuclei are in states

v_i , which are to be thermally averaged at the end. In the final state $|f\rangle$ with total energy E_f , the electron has momentum $\hbar\vec{k}_f$, the medium electrons remain in the ground state 0_e (because we are dealing with the subexcitation domain), and the nuclei are in state v_f (which differs from v_i). According to perturbation theory, the transition probability is written as

$$dw = (2\pi/\hbar) |A|^2 \delta(E_i - E_f) df, \quad (4)$$

where df represents the final-state density, and the transition amplitude A is given as

$$A = (f|V|i) + \int \frac{(f|V|s)(s|V|i)}{E_i - E_s} ds + \dots, \quad (5)$$

where $|s\rangle$ represents an intermediate state with total energy E_s and state density ds . More specifically, in the intermediate state $|s\rangle$ the electron has momentum $\hbar\vec{k}_s$, the medium electrons are in an excited state n , and the nuclei are in a state v_s .

The first-order term is expressed as

$$(f|V|i) = (e^2/2\pi^2 K^2) [(0_e, v_f | \sum_j e^{i\vec{K}\cdot\vec{r}_j} | 0_e, v_i) - (v_f | \sum_\lambda e^{i\vec{K}\cdot\vec{R}_\lambda} | v_i)], \quad (6)$$

with the momentum transfer $\hbar\vec{K} = \hbar\vec{k}_i - \hbar\vec{k}_f$. The first term in the square brackets is the nuclear matrix element of the *electronically elastic* form factor. We may express it as $(v_f | F(K; \vec{R}_\lambda) | v_i)$, where the electronic matrix element

$$F(K; \vec{R}_1, \vec{R}_2, \dots) = (0_e | \sum_j e^{i\vec{K}\cdot\vec{r}_j} | 0_e)$$

depends parametrically on the nuclear positions. If the dependence on $\vec{R}_\lambda$ is weak, the nuclear matrix element is governed by $\partial F(K; \vec{R}_1, \vec{R}_2, \dots) / \partial \vec{R}_\lambda$, evaluated at the nuclear equilibrium positions. The second term in the square brackets of Eq. (6) is a purely nuclear matrix element. Further properties of $(f|V|i)$ for gaseous molecules have been discussed by Itikawa¹⁴ and by Bonham and Geiger.¹⁵

The matrix elements in the second-order term of Eq. (5) are the following:

$$\begin{aligned} (s|V|i) &= (e^2/2\pi^2) |\bar{k}_i - \bar{k}_s|^{-2} (\bar{k}_s, n, v_s | \sum_j e^{i(\bar{k}_i - \bar{k}_s) \cdot \bar{r}_j} | \bar{k}_i, 0_e, v_i) \\ (f|V|s) &= (e^2/2\pi^2) |\bar{k}_s - \bar{k}_f|^{-2} (\bar{k}_f, 0_e, v_f | \sum_j e^{i(\bar{k}_s - \bar{k}_f) \cdot \bar{r}_j} | \bar{k}_s, n, v_s). \end{aligned} \quad (7)$$

The purely nuclear term vanishes here because $n_s \neq 0_e$. The energy denominator is

$$E_i - E_s = (\hbar^2/2m)(k_i^2 - k_s^2) + E(0_e, v_i) - E(n, v_s), \quad (8)$$

where $E(0_e, v_i)$ and $E(n, v_s)$ are the eigenvalues of H_m for either state. Note that the denominator never vanishes. The integral notation $\int ds$ in Eq. (5) is symbolic; its meaning may be explicitly given as $(2\pi)^{-3/2} \int d\bar{k}_s \sum_n \sum_{v_s}$.

With all quantities thus spelled out, we may define the longitudinal Raman matrix element $(\bar{k}_f, v_f | L_R | \bar{k}_i, v_i)$ as representing the second-order term of Eq. (5).

Remarks

The longitudinal Raman process also pertains to the energy loss of an ion at speeds comparable with, or less than, those of the medium electrons in the valence shell. Such an ion has generally a kinetic energy of keV's, far exceeding the electronic-excitation threshold, but its collisions are largely adiabatic and mostly result in elastic scattering, as Bohr¹⁶ explained. The direct momentum transfer upon elastic scattering is a main contributor to the energy loss of the ion. However, the longitudinal Raman process should also contribute. The expression for the L_R matrix element is formally the same as for a subexcitation electron, apart from an additional factor z^2 , where ze is the ion charge, and from the ion mass in the energy denominator, Eq. (8). A substantial difference between the ion and the subexcitation electrons lies in the magnitudes of the momenta involved, $\bar{k}_i$, $\bar{k}_f$, and $\bar{k}_s$.

Numerical evaluation of the longitudinal Raman matrix element requires knowledge of the whole spectrum of electronic excitations, or alternatively, of the corresponding Green's

function. Relevant knowledge is meager from either experiment or theory. Even within the dipole approximation, in which one regards $|\bar{k}_i - \bar{k}_s|$ and $|\bar{k}_s - \bar{k}_f|$ as small, the vectors $\bar{k}_i - \bar{k}_s$ and $\bar{k}_s - \bar{k}_f$ are not quite parallel, and therefore one deals with correspondingly different dipole matrix elements. Optical data on the ordinary Raman process pertain to negligibly small values of the momentum transfer transverse to the electric field.

Accordingly, this note aims at drawing experimentalists' attention to the task of measuring the longitudinal Raman matrix element. A possible experiment to this end may use grazing collisions of energy-resolved electrons or ions with a material surface. Analysis of the kinetic energies of scattered particles should carry pertinent information, although one would have to discount effects of surface properties.

References

1. R. L. Platzman, *Radiat. Res.* 2, 1 (1955).
2. M. Inokuti, in Molecular Processes in Space, edited by T. Watanabe, I. Shimamura, M. Shimizu, and Y. Itikawa (Plenum Publishing Corporation, New York, 1990) p. 65.
3. As fully explained, for instance, by K. Takayanagi in Electron-Molecule Collisions, edited by I. Shimamura and K. Takayanagi (Plenum Press, New York, 1984), p. 1, the earliest calculations on rotational excitation of a molecule by an electron were based on electrostatic interactions, viz., direct Coulomb interactions between the electron and the static charge distribution of the molecule, commonly expressed in terms of its multipole moments. In the 1960s, it began to be recognized that the polarization interactions resulting from the distortion of the electron cloud by the incoming electron are also important for rotational and vibrational excitation. The same idea was pursued further in the analysis of experiments by K.-H. Kochem, W. Sohn, K. Jung, H. Ehrhardt, and E. S. Chang, *J. Phys. B* 18, 1253 (1985), following theoretical work by E. S. Chang, *J. Phys. B* 17, 3341 (1984), who referred to the Raman mode.
4. G. J. Schulz, *Rev. Mod. Phys.* 49, 378 and 423 (1973).
5. J. A. Stephens and F. Robicheaux, *Radiat. Res.* 110, 19 (1987).

6. Earlier work is exemplified by L. Sanche, J. Chem. Phys. 71, 4860 (1979); L. Sanche and M. Michaud, Phys. Rev. B 30, 6078 (1984); and L. Sanche, and M. Michaud in Resonances in Electron-Molecule Scattering, van der Waals Complexes, and Reactive Chemical Dynamics, ACS Symposium Series 263, edited by D. G. Truhlar (American Chemical Society, Washington, D.C., 1984), p. 211. Recent work is seen in M. Michaud and L. Sanche, J. Electron Spectrosc. Rel. Phenom. 51, 237 (1990), and L. Sanche, in Excess Electrons in Dielectric Media, edited by C. Ferradini and J.-P. Jay-Gerin (CRC Press, Boca Raton, Florida, 1991), p. 1.
7. U. Fano, J. A. Stephens, and M. Inokuti, J. Chem. Phys. 85, 6239 (1986).
8. J. A. Stephens and U. Fano, Phys. Rev. A 38, 3371 (1988).
9. U. Fano and N.-Y. Du, Appl. Radiat. Isot. 42, 975 (1991).
10. D. L. Mills, Phys. Rev. B 45, 36 (1992); 45, 13221 (1992).
11. N. Bohr, Phil. Mag. 25, 10 (1913); 30, 581 (1915).
12. R. P. Feynman, Phys. Rev. 56, 340 (1939).
13. S. E. Schnatterly and C. Tarrio, Rev. Mod. Phys. 64, 619 (1992).
14. Y. Itikawa, in Argonne National Laboratory Radiological and Environmental Research Division Annual Report, ANL-8060, Part I, p. 87 (1973).
15. R. A. Bonham and J. Geiger, J. Chem. Phys. 51, 5246 (1969). See also R. A. Bonham, J. Chem. Phys. 62, 4586 (1975) for additional remarks and corrections.
16. N. Bohr, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. 18, No. 8 (1948).

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