PHYSICAL REVIEW A VOLUME 55, NUMBER 1 JANUARY 1997

Theory of gas-phase time-resolved ultrafast electron diffraction

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(Received 22 May 1996)

A theory of high-energy electron diffraction from diatomic molecular gases after excitation by a femtosecond laser is presented. Rotational and vibrational coherence created by the excitation pulse are taken into account. The use of the spherical tensor components of the density matrix along with the Liouville space formalism allows a systematic derivation of the resulting equations. [S1050-2947(97)08901-4]

PACS number(s): 34.50.Rk, 34.80.−i, 33.20.Sn, 33.20.Tp

I. INTRODUCTION

Recently, ultrafast electron diffraction experiments using a femtosecond laser system, a picosecond electron gun together with a two-dimensional charge-coupled device detection system, showed great promise for studying the temporal evolution of a gas-phase molecular system after coherent excitation [1,2]. In this paper, we present a formal theory for the electron diffraction from diatomic molecules after excitation by a femtosecond laser. The rotational and vibrational coherence effects created by the excitation processes are considered in detail.

We shall employ the density matrix formalism. The general theory of the pumping process by femtosecond pulses has been presented previously [3–5]. For rotational invariance considerations, the irreducible spherical tensor technique together with the Liouville space description are particularly appropriate. Such procedures were first used in pressure broadening studies [6,7] and have been extended to study various gas-phase relaxation processes [8–11]. Electron diffraction will be treated within the first Born approximation. However, since we are considering scattering from a superposition of states rather than a pure state, the usual expression for the differential cross section must be modified appropriately. The Born-Oppenheimer approximation is used, and the contributions from vibrational and rotational effects can be treated separately.

This paper is organized as follows: in Sec. II we present the theory of the femtosecond laser pumping process as applied to the vibrational-rotational states of a linear molecule, and by use of the Liouville space formalism we show how the tensorial components of the upper-state density matrix of different ranks are created by the excitation process. A brief description of the subsequent relaxation process is also discussed. In Sec. III, we consider the scattering of the electrons by the molecules in the mixed state resulting from the pumping and relaxation processes. A summary and conclusions will be presented in Sec. IV. In the Appendix we present an elementary derivation of the differential cross section for scattering from a mixed state.

II. EXCITATION AND RELAXATION OF LINEAR MOLECULES

The general theory of femtosecond laser excitation of a system has been presented previously [3,4], and we shall apply the results to the specific case of the electronic and vibrational-rotational states of a linear molecule. Under the dipole approximation, the interaction of the molecule with the quasimonochromatic radiation is given by

$$H_{int}(t)=[H'(\Omega)e^{-i\Omega t}+H'(-\Omega)e^{i\Omega t}]L(t), \tag{1}$$

where $H'(\Omega)=-\mathbf{d}\cdot\hat{\mathbf{e}}E(\Omega)$ with $\mathbf{d}$ being the molecular dipole matrix element, and $\hat{\mathbf{e}}$, Ω, $E(\Omega)$ being the polarization vector, the frequency, and the electric field amplitude of the laser radiation, respectively. $L(t)$ is the dimensionless pulse shape function satisfying

$$\int_{-\infty}^{\infty}L(t)dt=T, \tag{2}$$

where T is the pulse duration. Since the electromagnetic field is real, the field amplitude satisfies $E(-\Omega)=E(\Omega)^*$.

The jump in the electronic excited state density matrix elements can be obtained from perturbation theory as [3,4]

$$\Delta\sigma_{e\beta,e\beta'}=\frac{1}{\hbar^2}\sum_{\alpha,\alpha'}\rho_{g\alpha,g\alpha'}\hat{L}(\omega_{e\beta,g\alpha}-\Omega)H'_{e\beta,g\alpha}(\Omega)\times\hat{L}(\Omega-\omega_{e\beta',g\alpha'})H'_{e\beta',g\alpha'}(-\Omega), \tag{3}$$

where $\rho_{g\alpha,g\alpha'}$ is the initial density matrix element, and $\hat{L}(\omega)$ is the Fourier transform of $L(t)$,

$$\hat{L}(\omega)=\int_{-\infty}^{\infty}dt\,e^{i\omega t}L(t). \tag{4}$$

Often $L(t)$ is represented by the exponential form $L(t)=e^{-2|t|/T}$, for which $\hat{L}(\omega)=(4/T)/[\omega^2+(2/T)^2]$ becomes a Lorentzian function. In Eq. (3), the subscripts g,e denote the ground and excited electronic states, while α,β are collective indices denoting the vibrational-rotational levels in the electronic ground and excited states, respectively. $\hbar\omega_{e\beta,g\alpha}$ is the energy difference between the excited-state level $|e\beta\rangle$ and the ground-state level $|g\alpha\rangle$. In this paper, we shall only consider excited states which are bounded.

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For a diatomic molecule, the vibrational-rotational states can be denoted explicitly by $\alpha=\{v_\alpha j_\alpha m_\alpha\}$, where $v_\alpha, j_\alpha, m_\alpha$ represent the quantum numbers for vibrational, rotational, and its projection along a space-fixed z axis, respectively, and we shall write the density matrix elements $\Delta\sigma_{e\beta,e\beta'}$ and $\rho_{g\alpha,g\alpha'}$ as $\Delta\sigma(ev_\beta j_\beta m_\beta, ev'_\beta j'_\beta m'_\beta)$ and $\rho(gv_\alpha j_\alpha m_\alpha, gv'_\alpha j'_\alpha m'_\alpha)$. Furthermore, the dipole moment $\mathbf{d}=d(R)\hat{\mathbf{R}}$ lies along the direction of the relative interatomic coordinate $\mathbf{R}$. Within the Born-Oppenheimer approximation, neglecting vibration-rotation interaction, and ignoring the R dependence of the electronic dipole matrix element (Condon approximation), the interaction energy matrix element can be written as

$$H'_{e\beta,g\alpha}(\Omega)=-d_{eg}\langle ev_\beta|gv_\alpha\rangle\langle j_\alpha m_\alpha|\hat{\mathbf{R}}\cdot\hat{\mathbf{e}}|j_\beta m_\beta\rangle, \tag{5}$$

where d_{eg} is the electronic dipole matrix element, and $\langle ev_\beta|gv_\alpha\rangle$ is the Frank-Condon factor. Equation (3) then becomes

$$\begin{aligned}\Delta\sigma(ev_\beta j_\beta m_\beta, ev'_\beta j'_\beta m'_\beta)&=A\sum_{j_\alpha m_\alpha}\sum_{j'_\alpha m'_\alpha}\hat{L}(\omega_{e\beta,g\alpha}-\Omega)\hat{L}(\Omega-\omega_{e\beta',g\alpha'})\\&\quad\times\langle j_\beta m_\beta|\mathcal{E}|j'_\beta m'_\beta\rangle,\end{aligned} \tag{6}$$

where $A=|d_{eg}E(\Omega)|^2\langle ev_\beta|gv_\alpha\rangle\langle gv'_\alpha|ev'_\beta\rangle/\hbar^2$, and the excitation operator is given by

$$\begin{aligned}\mathcal{E}=\sum_{m_\alpha,m'_\alpha}&(\hat{\mathbf{R}}\cdot\hat{\mathbf{e}})|j_\alpha m_\alpha\rangle\rho(gv_\alpha j_\alpha m_\alpha, gv'_\alpha j'_\alpha m'_\alpha)\\&\times\langle j'_\alpha m'_\alpha|(\hat{\mathbf{R}}\cdot\hat{\mathbf{e}})^\dagger,\end{aligned} \tag{7}$$

which is a straightforward generalization of the excitation operator given in Refs. [8,12,13,10]. Following Ref. [10], this excitation operator can be written in terms of Liouville operators and the coupled Liouville basis as

$$\begin{aligned}|\mathcal{E}\rangle\rangle=\sum_{KQ}&\Phi^{(K)*}(\hat{\mathbf{e}})\mathcal{D}_Q^{(K)}(\hat{\mathbf{R}})\\&\times\sum_{K_\alpha Q_\alpha}\rho_{Q_\alpha}^{(K_\alpha)}(v_\alpha j_\alpha, v'_\alpha j'_\alpha)|j_\alpha(j'_\alpha)^+;K_\alpha Q_\alpha\rangle\rangle,\end{aligned} \tag{8}$$

where

$$\mathcal{D}_Q^{(K)}(\hat{\mathbf{R}})=\sum_{qq'}(-1)^{1-q}\sqrt{2K+1}\begin{pmatrix}1 & 1 & K\\ q & -q' & -Q\end{pmatrix}\hat{R}_q\otimes\hat{R}^*_{q'}, \tag{9}$$

$$\Phi_Q^{(K)}(\hat{\mathbf{e}})=\sum_{qq'}(-1)^{1+K-q}\sqrt{2K+1}\begin{pmatrix}1 & 1 & K\\ q & -q' & -Q\end{pmatrix}e_q e^*_{q'}, \tag{10}$$

in which $\hat{R}_q, \hat{e}_q$ are the spherical components of $\hat{\mathbf{R}}$ and $\hat{\mathbf{e}}$, respectively. The irreducible tensorial components are defined by

$$\begin{aligned}|j_\alpha(j'_\alpha)^+;K_\alpha Q_\alpha\rangle\rangle=\sum_{m_\alpha m'_\alpha}&(-1)^{j_\alpha-m_\alpha}\sqrt{2K_\alpha+1}\\&\times\begin{pmatrix}j_\alpha & j_\alpha & K_\alpha\\ m_\alpha & -m'_\alpha & -Q_\alpha\end{pmatrix}|j_\alpha m_\alpha\rangle\langle j_\alpha m'_\alpha|\end{aligned} \tag{11}$$

and

$$\begin{aligned}\rho_{Q_\alpha}^{(K_\alpha)}(v_\alpha j_\alpha, v'_\alpha j'_\alpha)=\sum_{m_\alpha m'_\alpha}&(-1)^{j_\alpha-m_\alpha}\sqrt{2K_\alpha+1}\\&\times\begin{pmatrix}j_\alpha & j'_\alpha & K_\alpha\\ m_\alpha & -m'_\alpha & -Q_\alpha\end{pmatrix}\\&\times\rho(v_\alpha j_\alpha m_\alpha, v'_\alpha j'_\alpha m'_\alpha),\end{aligned} \tag{12}$$

where the dependence on the electronic states has been suppressed.

The Liouville operator $\mathcal{D}_Q^{(K)}$ can be expanded in a complete set of Liouville basis as

$$\begin{aligned}\mathcal{D}_Q^{(K)}=\sum_{K_\alpha Q_\alpha}\sum_{K_\beta Q_\beta}\sum_{j_\alpha j'_\alpha}\sum_{j_\beta j'_\beta}&\\ \times\langle\langle j_\beta(j'_\beta)^+;K_\beta Q_\beta|\mathcal{D}_Q^{(K)}|j_\alpha(j'_\alpha)^+;K_\alpha Q_\alpha\rangle\rangle&\\ \times|j_\beta(j'_\beta)^+;K_\beta Q_\beta\rangle\rangle\langle\langle j_\alpha(j'_\alpha)^+;K_\alpha Q_\alpha|,&\end{aligned} \tag{13}$$

whose matrix elements satisfy the Wigner-Eckart theorem [13]

$$\begin{aligned}\langle\langle j_\beta(j'_\beta)^+;K_\beta Q_\beta|\mathcal{D}_Q^{(K)}|j_\alpha(j'_\alpha)^+;K_\alpha Q_\alpha\rangle\rangle&\\=(-1)^{K_\beta-Q_\beta}\begin{pmatrix}K_\beta & K & K_\alpha\\ -Q_\beta & Q & Q_\alpha\end{pmatrix}&\\ \times\langle\langle j_\beta j'^+_\beta K_\beta||\mathcal{D}^{(K)}||j_\alpha j'^+_\alpha K_\alpha\rangle\rangle.&\end{aligned} \tag{14}$$

The reduced matrix element is given by [10]

$$\begin{aligned}\langle\langle j_\beta j'^+_\beta K_\beta||\mathcal{D}^{(K)}||j_\alpha j'^+_\alpha K_\alpha\rangle\rangle&\\=\langle j_\beta||\hat{R}||j_\alpha\rangle\langle j'_\beta||\hat{R}||j'_\alpha\rangle^*[K_\beta K K_\alpha]^{1/2}&\\ \times\begin{Bmatrix}j_\beta & j_\alpha & 1\\ j'_\beta & j'_\alpha & 1\\ K_\beta & K_\alpha & K\end{Bmatrix}&\end{aligned} \tag{15}$$

and

$$\langle j_\beta||\hat{R}||j_\alpha\rangle=(-1)^{j_\beta}[j_\alpha j_\beta]^{1/2}\begin{pmatrix}j_\beta & 1 & j_\alpha\\ 0 & 0 & 0\end{pmatrix}. \tag{16}$$

Here, $[x_1, x_2, \ldots]$ denotes the product $(2x_1+1)(2x_2+1)\cdots$.

Similar to Eq. (12), irreducible tensorial components of the excited-state density matrix can be defined by

$$\Delta\sigma_{Q_\beta}^{(K_\beta)}(v_\beta j_\beta, v'_\beta j'_\beta) = \sum_{m_\beta m'_\beta} (-1)^{j_\beta - m_\beta}\sqrt{2K_\beta+1} \times \begin{pmatrix} j_\beta & j'_\beta & K_\beta \\ m_\beta & -m'_\beta & -Q_\beta \end{pmatrix} \times \Delta\sigma(ev_\beta j_\beta m_\beta, ev'_\beta j'_\beta m'_\beta). \tag{17}$$

Substituting Eqs. (6), (8), (13), and (14) into Eq. (17) then gives

$$\begin{aligned}\Delta\sigma_{Q_\beta}^{(K_\beta)}(v_\beta j_\beta, v'_\beta j'_\beta) &= A\sum_{j_\alpha j'_\alpha}\sum_{KQ}\sum_{K_\alpha Q_\alpha}\hat{L}(\omega_{e\beta,g\alpha}-\Omega) \\ &\times \hat{L}(\Omega-\omega_{e\beta',g\alpha'})\Phi_Q^{(K)}(\hat{\mathbf{e}})^* \\ &\times(-1)^{K_\beta-Q_\beta}\begin{pmatrix} K_\beta & K & K_\alpha \\ -Q_\beta & Q & Q_\alpha\end{pmatrix} \\ &\times\langle\langle j_\beta j'^{+}_\beta K_\beta \| \mathcal{D}^{(K)} \| j_\alpha j'^{+}_\alpha K_\alpha\rangle\rangle \\ &\times \rho_{Q_\alpha}^{(K_\alpha)}(v_\alpha j_\alpha, v'_\alpha j'_\alpha).\end{aligned} \tag{18}$$

Usually the initial state is isotropic, i.e.,

$$\rho(gv_\alpha j_\alpha m_\alpha, gv'_\alpha j'_\alpha m'_\alpha) = \rho_{gv_\alpha j_\alpha}\delta_{v_\alpha v'_\alpha}\delta_{j_\alpha j'_\alpha}\delta_{m_\alpha m'_\alpha}, \tag{19}$$

where $\rho_{gv_\alpha j_\alpha}$ is the Boltzmann distribution for the level $(gv_\alpha j_\alpha)$, yielding

$$\rho_{Q_\alpha}^{(K_\alpha)}(v_\alpha j_\alpha, v'_\alpha j'_\alpha) = \rho_{gv_\alpha j_\alpha}\sqrt{2j_\alpha+1}\,\delta_{v_\alpha v'_\alpha}\delta_{j_\alpha j'_\alpha}\delta_{K_\alpha 0}\delta_{Q_\alpha 0}. \tag{20}$$

In this case, Eq. (18) simplifies to

$$\begin{aligned}\Delta\sigma_Q^{(K)}(v_\beta j_\beta, v'_\beta j'_\beta) &= A\sum_{j_\alpha}\hat{L}(\omega_{e\beta,g\alpha}-\Omega)\hat{L}(\Omega-\omega_{e\beta',g\alpha'}) \\ &\times(-1)^K\Phi_Q^{(K)}(\hat{\mathbf{e}})^*[j_\beta j'_\beta]^{1/2}\begin{pmatrix} j_\alpha & j_\beta & 1 \\ 0 & 0 & 0\end{pmatrix} \\ &\times\begin{pmatrix} j_\alpha & j'_\beta & 1 \\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} 1 & j_\beta & j_\alpha \\ j'_\beta & 1 & K\end{Bmatrix}(2j_\alpha+1)\rho_{gv_\alpha j_\alpha}.\end{aligned} \tag{21}$$

Thus, the tensorial ranks of the excited state distribution are determined by the tensorial character of the dipole radiation. It is clear from Eq. (10) that K in general can take the values 0, 1, or 2. The dependence of the polarization of the pumping field is given by the factor $\Phi_Q^{(K)}$. For plane polarized radiation with the electric field along the space-fixed z direction, q and q' in Eq. (10) are zero, and K can only be 0 or 2. The Fourier transforms $\hat{L}$ determine the excited state levels that will be coherently pumped by the femtosecond laser.

Equation (18) or (20) establishes the initial conditions for the excited-state density matrix elements after the passage of the pumping pulse. In an isotropic environment, the relaxation of the upper-state levels can be described by a relaxation matrix $\Lambda^{(K)}$ which is diagonal in K,Q and independent of Q [7]. The equation of motion for the excited state density matrix is then given by

$$\frac{d}{dt}\rho_Q^{(K)}(b,b';t) = -i\omega_{b,b'}\rho_Q^{(K)}(b,b';t) - \sum_{\overline{b},\overline{b'}}\Lambda^{(K)}(b,b';\overline{b,b'})\rho_Q^{(K)}(\overline{b,b'};t), \tag{22}$$

with $\rho_Q^{(K)}(b,b';0)=\Delta\sigma_Q^{(K)}(b,b')$. Here b denotes collectively (v_β, j_β). $\hbar\omega_{b,b'}$ is the energy difference between the vibrational-rotational levels b and b' within the excited electronic manifold. Usually the inelastic transition rates are much less than the diagonal relaxation rates $\Lambda^{(K)}(b,b';b,b')$. Hence as a first approximation, we can ignore the relaxation matrix elements with $b\neq b$ and $b' \neq b'$ so that

$$\rho_Q^{(K)}(b,b';t) = \exp\{[-i\omega_{b,b'}-\Lambda^{(K)}(b,b';b,b')]t\} \times\Delta\sigma_Q^{(K)}(b,b'). \tag{23}$$

III. ELECTRON DIFFRACTION FROM DIATOMIC MOLECULES IN MIXED STATE

A. General considerations

In the time-resolved ultrafast electron diffraction experiments [1,2], the molecular system is pumped by a femtosecond laser pulse, so that an excited state distribution as given by Eq. (18) or (21) is prepared. After a time delay t_d in which the system in the excited-state manifold evolves according to Eq. (22), it is probed by high-energy (10–100 keV) electron diffraction. Since the system is in a mixed state described by the density matrix $\boldsymbol{\rho}$ with elements $\rho_Q^{(K)}(v_\beta j_\beta v'_\beta j'_\beta; t_d)$, the differential cross section for electron scattering is given by [14,15]

$$\frac{d\sigma}{d\Omega} = \left(\frac{m_e}{2\pi\hbar^2}\right)^2\frac{\mathrm{Tr}\,\mathbf{T}_{\mathbf{k'k}}\rho T^\dagger_{kk'}}{\mathrm{Tr}\boldsymbol{\rho}}, \tag{24}$$

where m_e is the mass of the electron. $\mathbf{T}_{\mathbf{k'k}}$ is the transition matrix for electron scattering from initial momentum $\hbar\mathbf{k}$ to final momentum $\hbar\mathbf{k}'$, and is related to the scattering amplitude by $\mathbf{f}_{\mathbf{k'k}}=(m_e/2\pi\hbar^2)\mathbf{T}_{\mathbf{k'k}}$. Equation (24) was originally used for spin-polarization considerations, and a derivation for the present situation is given in the Appendix.

At high energy, the transition matrix operator can be evaluated using the first Born approximation [14,15],

$$T_{\mathbf{k'k}} = \int d\mathbf{r}\,e^{-i\mathbf{q}\cdot\mathbf{r}}V(\mathbf{r},\mathbf{x},\mathbf{X}), \tag{25}$$

where $\mathbf{q}=\mathbf{k}'-\mathbf{k}$ is the momentum transfer, $\mathbf{r}$ is the position vector of the scattering electron, and $\mathbf{x},\mathbf{X}$ represent collectively the position vectors of the bound electrons and nucleus, respectively, of the molecule. For a diatomic molecule AB, the potential is

$$V(\mathbf{r},\mathbf{x},\mathbf{X}) = -\frac{Z_A e^2}{|\mathbf{r}-\mathbf{R}_A|} - \frac{Z_B e^2}{|\mathbf{r}-\mathbf{R}_B|} + \sum_i \frac{e^2}{|\mathbf{r}-\mathbf{r}_i|}, \tag{26}$$

where e is the electronic charge, $Z_n, \mathbf{R}_n$ are the atomic number and the position vector of the nucleus of atom n, respectively, and $\mathbf{r}_i$ is the position vector of the ith electron. Using the Fourier representation of the Coulomb interaction $(1/r) = (2\pi)^{-3} \int d\mathbf{K} (4\pi/K^2) \exp(i\mathbf{K}\cdot\mathbf{r})$, the transition matrix element becomes

$$T_{\mathbf{k}'\mathbf{k}} = \frac{4\pi}{q^2} \left(\sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i} - \sum_n Z_n e^{-i\mathbf{q}\cdot\mathbf{R}_n} \right). \tag{27}$$

As pointed out by Iijima *et al.* [16], the explicit expression for the cross section depends on the resolution of the electron detector. We shall explore different cases in the following subsections.

B. High-resolution detection

If the detector can resolve electrons scattered from individual or groups of molecular vibrational-rotational states, then for electronic elastic collisions, the trace in Eq. (24) is given explicitly by

$$\begin{aligned} \mathrm{Tr}\mathbf{T}_{\mathbf{k}'\mathbf{k}} \rho \mathrm{T}^{\dagger}_{\mathbf{k}\mathbf{k}'} = & \sum_{vjm} \sum_{v''j''m''} \sum_{v'j'm'}{}'' \langle ev'j'm' | T_{\mathbf{k}'\mathbf{k}} | evjm \rangle \\ & \times \langle vjm | \rho | v''j''m'' \rangle \\ & \times \langle ev'j'm' | T_{\mathbf{k}'\mathbf{k}} | ev''j''m'' \rangle^*, \end{aligned} \tag{28}$$

where the double prime over the sum over $v'j'm'$ implies only states falling within the energy resolution of the detector are included.

Next, we make the Born-Oppenheimer approximation and write the molecular wave function as

$$\phi_{evjm}(\mathbf{x},\mathbf{X}) = \psi_e(\mathbf{x};\mathbf{X}) \chi_{evjm}(\mathbf{X}), \tag{29}$$

where the electronic wave function ψ_e depends on the nuclear coordinates $\mathbf{X}$ parametrically. The transition matrix element between the electronic states can then be expressed in terms of the electron density $\rho(\mathbf{r})$ by

$$\langle \psi_e | T_{\mathbf{k}'\mathbf{k}} | \psi_e \rangle = \frac{4\pi}{q^2} \left\{ \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \rho(\mathbf{r}) - \sum_n Z_n e^{-i\mathbf{q}\cdot\mathbf{R}_n} \right\}, \tag{30}$$

where

$$\rho(\mathbf{r}) = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N |\psi_e(\mathbf{r}_1 \cdots \mathbf{r}_N)|^2 \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i), \tag{31}$$

and $N = Z_A + Z_B$ is the total number of electrons of the molecule. Within the independent-atom approximation (IAA), the electronic wave function ψ_e is expressed as the product of atomic orbitals $\phi_{A1} \cdots \phi_{AZ_A} \phi_{B1} \cdots \phi_{BZ_B}$ where ϕ_{Ai} and ϕ_{Bj} are atomic orbitals centered on atoms A and B, respectively. Then

$$\rho(\mathbf{r}) = \sum_{n=A,B} \rho_n(\mathbf{r}-\mathbf{R}_n), \tag{32}$$

where

$$\rho_n(\mathbf{r}) \equiv \sum_{i=1}^{Z_n} \int d\mathbf{r}_{in} |\phi_{ni}(\mathbf{r}_{in})|^2 \delta(\mathbf{r}-\mathbf{r}_{in}) \tag{33}$$

with $\mathbf{r}_{in} = \mathbf{r}_i - \mathbf{R}_n$. The same result can be obtained if ψ_e is represented in terms of a Slater determinant of linear combination of atomic orbitals–molecular orbitals (LCAO-MO's) and overlap integrals are neglected [17]. The IAA has been shown to be adequate for structural analysis [16]. The transition matrix element of Eq. (30) then simplifies to

$$T_{\mathbf{k}'e,\mathbf{k}e} \equiv \langle \psi_e | T_{\mathbf{k}'\mathbf{k}} | \psi_e \rangle = \frac{4\pi}{q^2} \sum_n [F_n(\mathbf{q}) - Z_n] e^{-i\mathbf{q}\cdot\mathbf{R}_n}, \tag{34}$$

where the atomic structure factors are given by $F_n(\mathbf{q}) = \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \rho_n(\mathbf{r})$.

Taking the origin at the center-of-mass of the diatomic molecule and defining the relative coordinate by $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$, the matrix element of the expression in Eq. (34) between vibrational-rotational states becomes

$$\begin{aligned} & \langle ev'j'm' | T_{\mathbf{k}'\mathbf{k}} | evjm \rangle \\ & \quad = \frac{4\pi}{q^2} \{ [F_A(\mathbf{q}) - Z_A] \langle v'j'm' | e^{-i(\mu/m_A)\mathbf{q}\cdot\mathbf{R}} | vjm \rangle \\ & \qquad + [F_B(\mathbf{q}) - Z_B] \langle v'j'm' | e^{i(\mu/m_B)\mathbf{q}\cdot\mathbf{R}} | vjm \rangle \}, \end{aligned} \tag{35}$$

where m_A, m_B are the masses of the atom A and B, respectively, and $\mu = m_A m_B / (m_A + m_B)$ is the reduced mass of the system. The matrix elements in Eq. (31) can be evaluated by using the expansion [18]

$$\exp(\pm i\mathbf{s}\cdot\mathbf{R}) = 4\pi \sum_{LM} (\pm i)^L j_L(sR) Y_{LM}(\hat{\mathbf{R}}) Y^*_{LM}(\hat{\mathbf{s}}), \tag{36}$$

where j_L and Y_{LM} are the spherical Bessel function and the spherical harmonics, respectively. Ignoring vibration-rotation interaction, we obtain

$$\begin{aligned} & \langle ev'j'm' | T_{\mathbf{k}'\mathbf{k}} | evjm \rangle \\ & \quad = \sum_{LM} i^L G_L(v',v) (-1)^{m'} [j'Lj]^{1/2} \begin{pmatrix} j' & L & j \\ 0 & 0 & 0 \end{pmatrix} \\ & \qquad \times \begin{pmatrix} j' & L & j \\ -m' & M & m \end{pmatrix} Y^*_{LM}(\hat{\mathbf{q}}), \end{aligned} \tag{37}$$

where

$$G_L(v',v)=\frac{(4\pi)^{3/2}}{q^2}\{(-1)^L[F_A(\mathbf{q})-Z_A]\langle v'|j_L(s_AR)|v\rangle +[F_B(\mathbf{q})-Z_B]\langle v'|j_L(s_BR)|v\rangle\} \tag{38}$$

and $s_i=(\mu/m_i)q,\ i=A,B$. The vibrational-dependent part can be simplified by making a first-order expansion of the spherical Bessel function about the equilibrium separation R_0 so that

$$\langle v'|j_L(s_iR)|v\rangle \simeq j_L(s_iR_0)\delta_{vv'}+s_i\langle v'|u|v\rangle j_L'(s_iR_0), \tag{39}$$

where $u=R-R_0$. For a simple harmonic oscillator with natural frequency ω_0, $\langle v'|u|v\rangle=(\hbar/2\mu\omega_0)^{1/2}(\delta_{v',v+1}\sqrt{v'}+\delta_{v',v-1}\sqrt{v'+1})$.

Substituting Eq. (37) into Eq. (28) and transforming the density matrix elements into the irreducible tensorial component similar to Eq. (12), we obtain

$$\begin{aligned}\mathrm{Tr}\mathbf{T}_{\mathbf{k}'\mathbf{k}}\rho\mathbf{T}^{\dagger}_{\mathbf{k}\mathbf{k}'}=&\sum_{KQ}\sum_{v'j'}{}''\sum_{vj}\sum_{v''j''}\sum_{LM}\sum_{L'M'} i^{L-L'}\\ &\times G_L(v',v)G_{L'}(v',v'')Y_{LM}(\hat{\mathbf{q}})Y_{L'M'}(\hat{\mathbf{q}})\\ &\times[j'Lj]^{1/2}[j'L'j''K]^{1/2}(-1)^{j'+j''}\\ &\times\begin{pmatrix} j' & L & j\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} j' & L' & j''\\ 0 & 0 & 0\end{pmatrix}\\ &\times\begin{pmatrix} L' & K & L\\ -M' & Q & -M\end{pmatrix}\begin{Bmatrix} L' & K & L\\ j & j' & j''\end{Bmatrix}\\ &\times\rho_Q^{(K)}(vj,v''j'';t_d).\end{aligned} \tag{40}$$

Explicit expression for the differential cross section can then be obtained from Eq. (24).

C. Medium-resolution detection

If the detector selects electrons which excite the same final electronic state of the molecule and all vibrational-rotational states with equal efficiency, the scattering intensity is proportional to an expression similar to Eq. (28), except that the sum over $(v'j'm')$ is over the *complete* set of vibrational-rotational states. By completeness, $\Sigma_{v'j'm'}|v'j'm'\rangle\langle v'j'm'|=1$, and we have

$$\mathrm{Tr}\mathbf{T}_{\mathbf{k}'\mathbf{k}}\rho\mathbf{T}^{\dagger}_{\mathbf{k}\mathbf{k}'}=\sum_{vjm}\sum_{v''j''m''}\langle vjm|\rho|v''j''m''\rangle \times\langle v''j''m''|T^{\dagger}_{\mathbf{k}e,\mathbf{k}'e}T_{\mathbf{k}'e,\mathbf{k}e}|vjm\rangle. \tag{41}$$

Substituting the IAA result of Eq. (34) into Eq. (41) and using the expansion of Eq. (36) with **s** replaced by **q**, we obtain after some algebra the result

$$\begin{aligned}\mathrm{Tr}\mathbf{T}_{\mathbf{k}'\mathbf{k}}\rho T^{\dagger}_{kk'}=&\left(\frac{4\pi}{q^2}\right)^2\Bigg\{[|F_A-Z_A|^2+|F_B-Z_B|^2]\\ &\times\sum_{vj}\sqrt{2j+1}\rho_0^{(0)}(vj,vj;t_d)\\ &+\sqrt{4\pi}\sum_{KQ}\sum_{vj}\sum_{v''j''}\langle v''|j_K(qR)|v\rangle[(-i)^K\\ &\times Y^*_{KQ}(\hat{\mathbf{q}})(F_A-Z_A)(F_B-Z_B)^*+\text{c.c.}]\\ &\times(-1)^j[jj'']^{1/2}\begin{pmatrix} j'' & K & j\\ 0 & 0 & 0\end{pmatrix}\\ &\times\rho_Q^{(K)}(vj,v''j'';t_d)\Bigg\},\end{aligned} \tag{42}$$

where c.c. denotes complex conjugation. The vibrational dependence can be simplified similar to Eq. (39).

For the case that all the molecules are prepared in a pure state v_ij_i, the density matrix elements in Eq. (42) becomes $\rho_Q^{(K)}(vj,v''j'')=\delta_{vv_i}\delta_{jj_i}\delta_{vv''}\delta_{jj''}\delta_{K0}\delta_{Q0}\sqrt{(2j_i+1)}$, and Eq. (42) reduces to

$$\begin{aligned}\mathrm{Tr}\mathbf{T}_{\mathbf{k}'\mathbf{k}}\rho\mathbf{T}^{\dagger}_{\mathbf{k}\mathbf{k}'}=&\left(\frac{4\pi}{q^2}\right)^2(2j_i+1)\{[|F_A-Z_A|^2+|F_B-Z_B|^2]\\ &+[(F_A-Z_A)(F_B-Z_B)^*+\text{c.c.}]\\ &\times\langle v_i|j_0(qR)|v_i\rangle\},\end{aligned} \tag{43}$$

the conventional expression for the electron scattering intensity by diatomic molecules [16,19].

D. Low-resolution detection

Finally, if the detector accepts electrons scattered from all final vibronic states of the molecule, the intensity is proportional to

$$\begin{aligned}\mathrm{Tr}\mathbf{T}_{\mathbf{k}'\mathbf{k}}\rho\mathrm{T}^{\dagger}_{\mathbf{k}\mathbf{k}'}=&\sum_{vjm}\sum_{v''j''m''}\sum_{e'v'j'm'}\\ &\times\langle e'v'j'm'|T_{\mathbf{k}'\mathbf{k}}|ev''j''m''\rangle^*\\ &\times\langle e'v'j'm'|T_{\mathbf{k}'\mathbf{k}}|evjm\rangle\langle vjm|\rho|v''j''m''\rangle\\ =&\sum_{vjm}\sum_{v''j''m''}\langle vjm|\rho|v''j''m''\rangle\\ &\times\langle ev''j''m''|T^{\dagger}_{\mathbf{k}\mathbf{k}'}T_{\mathbf{k}'\mathbf{k}}|evjm\rangle,\end{aligned} \tag{44}$$

where in the last equality, the completeness of the vibronic states $(e'v'j'm')$ has been used. Using Eq. (27), the electronic matrix element of the bilinear product of the transition matrix can be expressed as

$$\begin{aligned}\langle\psi_e|T^{\dagger}_{\mathbf{kk}'}T_{\mathbf{k}'\mathbf{k}}|\psi_e\rangle\\ =\left(\frac{4\pi}{q^2}\right)^2\Bigg\{(Z_A+Z_A^2+Z_B+Z_B^2)+\int d\mathbf{r}\rho_c(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}\\ +\Bigg[Z_AZ_Be^{-i\mathbf{q}\cdot\mathbf{R}}-\left(\sum_{n=A,B}Z_ne^{i\mathbf{q}\cdot\mathbf{R}_n}\right)\\ \times\int d\mathbf{r}\rho(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}+\text{c.c.}\Bigg]\Bigg\},\end{aligned}\qquad(45)$$

where $\rho(\mathbf{r})$ is given by Eq. (31) and the second-order electron density function is defined by [20]

$$\rho_c(\mathbf{r})=\int d\mathbf{r}_1\cdots d\mathbf{r}_N|\psi_e(\mathbf{r}_1\cdots\mathbf{r}_N)|^2\sum_{i\neq j}^{N}\delta(\mathbf{r}-\mathbf{r}_i+\mathbf{r}_j).\qquad(46)$$

Within the IAA, $\rho(\mathbf{r})$ is given by Eq. (32), while the Fourier transform of $\rho_c(\mathbf{r})$ can be expressed as

$$\int d\mathbf{r}\rho_c(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}=[F_A(\mathbf{q})F_B^*(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}}+\text{c.c.}]-\Delta,\qquad(47)$$

where

$$\Delta=\sum_{n=A,B}\sum_{i=1}^{Z_n}|\langle\phi_{ni}|e^{-i\mathbf{q}\cdot\mathbf{r}_{in}}|\phi_{ni}\rangle|^2\qquad(48)$$

is independent of the nuclear coordinates $\mathbf{R}_A$ and $\mathbf{R}_B$. Substituting Eqs. (32) and (47) into Eq. (45) and proceeding as before, we can reduce Eq. (44) to the final result

$$\begin{aligned}\mathrm{Tr}\mathbf{T}_{\mathbf{k}'\mathbf{k}}\rho\mathrm{T}^{\dagger}_{\mathbf{kk}'}=\left(\frac{4\pi}{q^2}\right)^2\Bigg\{\sum_{vj}\sqrt{2j+1}\rho_0^{(0)}(vj,vj;t_d)\mathcal{G}_i\\ +\sqrt{4\pi}\sum_{KQ}\sum_{vj}\sum_{v''j''}\langle v''|j_K(qR)|v\rangle\\ \times[(-i)^KY^*_{KQ}(\hat{\mathbf{q}})\mathcal{G}_c+\text{c.c.}]\\ \times(-1)^j[jj'']^{\frac{1}{2}}\begin{pmatrix}j'' & K & j\\ 0 & 0 & 0\end{pmatrix}\\ \times\rho_Q^{(K)}(vj,v''j'';t_d)\Bigg\},\end{aligned}\qquad(49)$$

where $\mathcal{G}_i=Z_A+Z_A^2+Z_B+Z_B^2+\Sigma_n\{|F_n(\mathbf{q})|^2-Z_n[F_n(\mathbf{q})+F_n^*(\mathbf{q})]\}-\Delta$, and $\mathcal{G}_c=Z_AZ_B+F_AF_B^*-Z_AF_B^*-Z_BF_A^*$. Again, if the molecules are initially in a pure state, Eq. (49) will reduce to the conventional result [20] similar to Eq. (43).

IV. SUMMARY AND DISCUSSIONS

In this paper, we have employed the Liouville space formalism to derive explicit expression for the irreducible tensorial components of the density matrix produced by a femtosecond pumping laser. Such tensorial components are particularly convenient for the consideration of relaxation in an isotropic environment. The main results are given by Eqs. (21) and (22). For subsequent probing of the system by electron diffraction, the coherence created by the pumping and relaxation processes can be taken into account by considering the transformation of the whole density matrix by the collision processes. For high-energy electron scattering, the first Born approximation can be used to evaluate the scattering amplitudes. The result for elastic collision in which the vibrational-rotational levels can be resolved is given by Eq. (40). The vectorial coupling of various angular momenta is clearly demonstrated by the Wigner 6-j symbol appearing in Eq. (40). Thus, the rotational angular momenta of the molecule, $\mathbf{j}$ and $\mathbf{j}'$, couple to form $\mathbf{K}$ whose magnitude gives the tensorial rank of the rotational coherence of the system. Due to the collision with the probing electron, the intermediate rotational angular momentum $\mathbf{j}'$ is produced by either coupling of $\mathbf{j}$ with the angular component $\mathbf{L}$ of the Coulomb interaction, or by coupling of $\mathbf{j}''$ with the component $\mathbf{L}'$. To conserve angular momentum, the components $\mathbf{L}$ and $\mathbf{L}'$ couple vectorially to form $\mathbf{K}$ again. Information on the structure of the molecule after initial excitation is contained in the factors G_L and $G_{L'}$. By measuring the electron diffraction pattern at different time delay t_d, information on the *excited state* relaxation dynamics can be obtained from the last factor of Eq. (40), $\rho_Q^{(K)}(vj,v''j'';t_d)$.

For medium- and low-resolution detection of the scattered electrons, the dependence on the rotational and vibrational states of the molecule is identical, as given by Eq. (42) and Eq. (49), and is *simpler* than the case of high-resolution detection. The electronic contributions to these two cases, of course, are different. Here, the angular dependence of the momentum transfer $\mathbf{q}$ is determined by the spherical harmonics with exactly the same order as the tensorial character of the coherence of the molecular system. If the molecules are prepared in a pure state, only the $(K,Q)=(0,0)$ component of the density matrix is nonvanishing, which corresponds to the population of the initial state, and the results reduce to the conventional expressions for electron scattering intensities. Thus, in this case there appears to be no advantage in using high resolution electron detection to study the coherence dynamics of the molecules.

ACKNOWLEDGMENTS

W.-K.L. thanks the Institute of Atomic and Molecular Sciences, Academia Sinica, for its hospitality. This work is supported by the NSC of the Republic of China and the NSERC of Canada.

APPENDIX: ELECTRON SCATTERING FROM MOLECULES IN A MIXED STATE

Consider the scattering of an electron beam, with incident momentum peaked at $\hbar\mathbf{k}_0$, by a molecule in the superposition state $\Sigma_\beta a_\beta\phi_\beta$. We shall derive Eq. (24) following the Lippmann-Schwinger equation approach discussed in Chap. 7 of Rodberg and Thaler [15], with suitable generalization. The incident beam can be represented by the wave packet

$$|\phi(t)\rangle=\sum_\beta\int\frac{d^3\mathbf{k}}{(2\pi)^3}A(\mathbf{k})a_\beta|\phi_{\mathbf{k}\beta}\rangle e^{-iE_{k\beta}t/\hbar}\qquad(A1)$$

where the amplitude function $A(\mathbf{k})$ is sharply peaked at $\mathbf{k}=\mathbf{k}_0$, $\phi_{\mathbf{k}\beta}=\phi_\beta \exp(i\mathbf{k}\cdot\mathbf{r})$, and $E_{k\beta}=E_k+\epsilon_\beta$ with ϵ_β and $E_k=\hbar^2k^2/2m_e$ being the molecular energy in state β and the electron kinetic energy, respectively. The total wave function is then given by

$$|\psi(t)\rangle=\sum_\beta \int \frac{d^3\mathbf{k}}{(2\pi)^3}A(\mathbf{k})a_\beta|\psi^+_{\mathbf{k}\beta}\rangle e^{-iE_{k\beta}t/\hbar}, \tag{A2}$$

where $|\psi^+_{\mathbf{k}\beta}\rangle$ satisfies the Lippmann-Schwinger equation

$$|\psi^+_{\mathbf{k}\beta}\rangle=|\phi_{\mathbf{k}\beta}\rangle+(E_{k\beta}-H_0+i0^+)^{-1}V|\psi^+_{\mathbf{k}\beta}\rangle, \tag{A3}$$

in which H_0 is the Hamiltonian of the noninteracting system. The second term of Eq. (A3) when substituted into Eq. (A2) gives rise to the scattered wave $\psi_{sc}(t)$, which behaves asymptotically as

$$\lim_{t\to\infty}|\psi_{sc}(t)\rangle=-2\pi i\sum_\beta \int \frac{d^3\mathbf{k}}{(2\pi)^3}A(\mathbf{k})a_\beta\delta(E_{k\beta}-H_0)V \times|\psi^+_{\mathbf{k}\beta}\rangle e^{-iE_{k\beta}t/\hbar}, \tag{A4}$$

since only poles on the real energy axis contribute to $\psi_{sc}(t)$ as $t\to\infty$ [15].

The probability of detecting the electrons scattered into the momentum range $\Delta k'$ is given by

$$P_{\Delta k'}=\lim_{t\to\infty}\sum_{\beta'} \int_{\Delta k'}\frac{d^3\mathbf{k}'}{(2\pi)^3}|\langle\phi_{\mathbf{k}'\beta'}e^{-iE_{\mathbf{k}'\beta'}t/\hbar}|\psi_{sc}(t)\rangle|^2. \tag{A5}$$

Substituting Eq. (A4) into Eq. (A5), defining the transition matrix element by

$$T_{\mathbf{k}'\beta',\mathbf{k}\beta}=\langle\phi_{\mathbf{k}'\beta'}|V|\psi^+_{\mathbf{k}\beta}\rangle \tag{A6}$$

and recognizing that it is a slowly varying function of **k** so that it can be replaced by $T_{\mathbf{k}'\beta',\mathbf{k}_0\beta}$, and ignoring the energy differences between the different vibrational-rotational levels within the wave packet compared to the kinetic energy of the scattering electron, the probability of Eq. (A5) becomes

$$P_{\Delta k'}=\frac{m_ek'}{(2\pi)^3\hbar^2}d\Omega \times\sum_{\beta\beta'\beta''}T_{\mathbf{k}'\beta',\mathbf{k}_0\beta}a_\beta a^*_{\beta''}T^*_{\mathbf{k}'\beta',\mathbf{k}_0\beta''}(2\pi)^2 \times\int\frac{d^3\mathbf{k}_1}{(2\pi)^3}\int\frac{d^3\mathbf{k}_2}{(2\pi)^3}A(\mathbf{k}_1)A(\mathbf{k}_2)^*\delta(E_{k_1}-E_{k_2}). \tag{A7}$$

Since the incident flux is given by

$$j_{inc}=\frac{\hbar k_0}{m_e}\int_{-\infty}^{\infty}\int d\mathbf{x}\int d\mathbf{X}|\langle\mathbf{rxX}|\phi(t)\rangle|^2_{\mathbf{r}=\mathbf{0}} =\frac{2\pi\hbar^2k_0}{m_e}\sum_\beta|a_\beta|^2\int\frac{d^3\mathbf{k}_1}{(2\pi)^3}\int\frac{d^3\mathbf{k}_2}{(2\pi)^3} \times A(\mathbf{k}_1)A(\mathbf{k}_2)^*\delta(E_{k_1}-E_{k_2}), \tag{A8}$$

dividing Eq. (A7) by Eq. (A8) gives the differential cross section

$$\frac{d\sigma}{d\Omega}=\left(\frac{m_e}{2\pi\hbar^2}\right)^2\frac{k'}{k_0} \times\sum_{\beta\beta'\beta''}T_{\mathbf{k}'\beta',\mathbf{k}_0\beta}a_\beta a^*_{\beta''}T^*_{\mathbf{k}'\beta',\mathbf{k}_0\beta''}\Big/\sum_\beta|a_\beta|^2. \tag{A9}$$

Realizing that at high electron energy, $k'\simeq k_0$, and the density matrix elements are defined by $\rho_{\beta\beta''}=a_\beta a^*_{\beta''}$, Eq. (24) follows immediately from Eq. (A9).

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