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Electronic Raman Spectra. III. Absolute Cross Sections for Electronic Raman and Rayleigh Scattering*

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Absolute cross sections for Rayleigh and electronic Raman scattering of trivalent rare-earth ions have been calculated. A comparison with the experimental cross section for benzene reveals that both the Rayleigh and Raman scattering for the lanthanides is weaker by more than two orders of magnitude. The Rayleigh-to-Raman ratio is shown to be a rapidly fluctuating function of the electronic structure of the lanthanide ions.

I. INTRODUCTION

ABSOLUTE cross sections of Raman scattering have been reported only in a very few cases.[1] Experimentally the determination of absolute cross sections is a tricky problem and any theoretical treatment of the absolute intensity problem for vibrational Raman transitions is extremely cumbersome.

Recently the theory of two-photon processes in trivalent lanthanide ions have been formulated[2–6] in some detail, making it possible to calculate, to a relatively high degree of accuracy, absolute cross sections for electronic scattering. Thus, in this paper we want to report on such calculations for free trivalent lanthanide ions.

II. THEORY

In a scattering experiment where the incident light is polarized in the direction σ and the scattered radiation is polarized in the direction ρ and where the direction of propagation of incident and scattered radiation are perpendicular to each other, the scattered intensity, according to Placzek,[7] will be given by

$$I_{kn}(\rho)=16\pi^4/\lambda'^4r^2|(\alpha_{\rho\sigma})_{kn}|^2I_0\sin^2\theta. \qquad (1)$$

Here λ' is the wavelength of the scattered radiations, r is the distance between the observer and the scattering system, $(\alpha_{\rho\sigma})_{kn}$ is the scattering tensor corresponding to the quantum transition $k\rightarrow n$, and θ is equal to $\frac{1}{2}\pi$.

For a scattering system that is freely rotating in space, the scattering tensor must be averaged over all directions of the rotating system. Thus, the results of this averaging (see Appendix I) are

$$I_{kn}(\rho)=\frac{16\pi^4}{\lambda'^4r^2}\sum_{KQ}(c_{\rho\sigma}{}^K)(\alpha_Q{}^K)^2\frac{1}{2K+1}I_0\sin^2\theta. \qquad (2)$$

The coefficients $c_{\rho\sigma}{}^K$ are also defined in the Appendix I. If the initial and/or final states k and n are degenerate, then Eq. (2) must be summed over all substates and the summation must be weighted with an additional factor $2g_k{}^{-1}$, where g_k is the degeneracy of the initial state k.

It is customary to define the total cross section $\bar{Q}_{kn}$ in terms of the total scattered intensity I_{tot} (for fixed polarization of incident light):

$$I_{\text{tot}}=\bar{Q}_{kn}I_0.$$

I_{tot} is related to $I_{kn}(\rho)$ in the following way:

$$I_{\text{tot}}=\sum_\rho\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}I_{kn}(\rho)r^2\sin\theta d\theta d\varphi. \qquad (3)$$

By substituting Eq. (2) in Eq. (3), we then have

$$\bar{Q}_{kn}=\frac{2^7\pi^5}{9\lambda'^4}\sum_K\sum_Q|(\alpha_Q{}^K)|^2. \qquad (4)$$

In order to proceed with the calculation of the absolute intensities one must be able to evaluate the tensor components $\alpha_Q{}^K$.

In case our scattering system is such that the angular momentum, as well as its projection upon some particular axis are constants of motion, a significant simplification can be made. According to Placzek,[7] the quantity $\alpha_Q{}^K$ must transform as the matrix element $\langle\psi_n|\hat{\alpha}_Q{}^K|\psi_k\rangle$. If the states n and k are characterized by the quantum numbers J', M' and J, M, respectively, we can use the Wigner-Eckart theorem[8] and get

$$\langle\psi_{M'}{}^{J'}|\alpha_Q{}^K|\psi_M{}^J\rangle =(-1)^{J'-M'}\begin{pmatrix}J' & K & J\\ -M' & Q & M\end{pmatrix}\langle J'\|\hat{\alpha}^K\|J\rangle. \qquad (5)$$

Consequently,

$$\sum_Q\sum_M\sum_{M'}(\alpha_Q{}^K)^2{}_{J,M;J'M'} =\langle J'\|\hat{\alpha}^K\|J\rangle^2\sum_Q\sum_M\sum_{M'}\begin{pmatrix}J' & K & J\\ -M' & Q & M\end{pmatrix}^2, \qquad (6)$$

$$=\langle J'\|\alpha^K\|J\rangle^2, \qquad (7)$$

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[1] See H. W. Schrötter and H. J. Bernstein, J. Mol. Spectry. 12, 1 (1964).

[2] J. D. Axe, Jr., Phys. Rev. **136**, A42 (1964).

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[5] O. Sonnich Mortensen and J. A. Koningstein, Chem. Phys. Letters **1**, 409 (1967).

[6] O. Sonnich Mortensen and J. A. Koningstein (to be published).

[7] G. Placzek, *Handbuch der Radiologie* (Leipzig, 1934), Vol. VI, Ser. II, p. 205.

[8] See, for instance, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N. J., 1960).

because of the orthonormality of the 3-j symbols.[8] The right-hand side of Eq. (7) is the reduced matrix element of the irreducible tensor operator of rank K.

III. RAYLEIGH AND RAMAN SCATTERING

For the special case of scattering by trivalent lanthanides, a quantitative theory for the absolute intensities has been derived.[2–6] It follows directly from the theory[6] that the reduced matrix element $\langle J'\|\alpha^K\|J\rangle$ is given by

$$\langle J'\|\alpha^K\|J\rangle=\langle\gamma'SL'J'\|U^K\|\gamma SLJ\rangle F(\gamma,\nu)\,, \tag{8}$$

where

$$F(K,\nu)=\frac{1}{h}(-1)^{K+1}(2K+1)^{1/2}\sum_x (l\|c^{(1)}\|l')^2\begin{Bmatrix}1 & K & 1\\ l & l' & l\end{Bmatrix}$$
$$\times\Bigg((nl|r|n'l')^2\left[\frac{1}{\bar{\nu}_{xk}-\nu}+\frac{(-1)^K}{\bar{\nu}_{xn}+\nu}\right]$$
$$+(nl|r|n'l')^2\left[\frac{\bar{\nu}_{xk}}{(\bar{\nu}_{xk}-\nu)^2}+\frac{(-1)^K\bar{\nu}_{xn}}{(\bar{\nu}_{xn}+\nu)^2}\right]$$
$$-\frac{(nl|r|n'l')(n'l'|[\mathcal{H}r]^r|nl)}{h\cdot(\bar{\nu}_{xk}-\nu)^2}$$
$$+(-1)^K\frac{(nl|[\mathcal{H}r]^r|n'l')(n'l'|r|nl)}{h\cdot(\bar{\nu}_{xn}+\nu)^2}\cdots\Bigg).$$

Here $\langle\gamma'SL'J'\|U^K\|\gamma SLJ\rangle$ is the reduced matrix element of the unit tensor of rank K. $\tilde{\nu}_{xk}$ is the center-of-gravity energy of the excited states configuration $|n'l'\rangle$, and $(nl|r|n'l')$ stands for the integral

$$\int R_{nl}rR_{n'l'}d\tau\,,$$

where R_{nl} is the radial wave function of the orbital nl.

The reduced matrix element $(l\|c^{(1)}\|l')$ is given by Edmonds[8] and the symbol $[\mathcal{H}r]^r$ stands for the radial part of the commutator of the Hamiltonian and the electronic position operator.

Since U is an orbital operator, the reduced matrix element can be expressed in terms of reduced matrix elements which involve only S and L. Using Eq. 7.1.8 of Edmonds,[8]

$$\langle\gamma'SL'J'\|U^K\|\gamma SLJ\rangle$$
$$=(-1)^{S+L+J'+K}[(2J+1)(2J'+1)]^{1/2}$$
$$\times\begin{Bmatrix}L' & J' & S\\ J & L & K\end{Bmatrix}\langle\gamma'SL'\|U^K\|\gamma SL\rangle\,, \tag{9}$$

the quantity $\langle\gamma SL'\|U^K\|\gamma SL\rangle$ has been tabulated by Nielson and Koster.[9]

TABLE I. Absolute cross sections[a] of Rayleigh and electronic Raman scattering for Pr^{3+} and Tm^{3+} ions.

Ion	Rayleigh	Raman	Raman transition
Pr^{3+}	0.9×10^{-29} cm^2	0.6×10^{-31}	$^3H_4\rightarrow{}^3H_5$
Tm^{3+}	1.3×10^{-30} cm^2	0.2×10^{-34}	$^3H_6\rightarrow{}^3H_4$

[a] Calculated for 6328 Å primary radiation.

In the summation over the excitated configuration x [Eq. (8)] we can in first approximation restrict our attention to the $(4f)^{n-1}(5d)$ configuration.[3] Since $\nu_{rk}-\tilde{\nu}_{xk}/\tilde{\nu}_{xk}-\nu\ll1$, only the first term in the expansion of the energy denominators needs to be considered.[10] The center-of-gravity energy for the $(4f)^{n-1}(5d)$ configuration may be estimated from the paper of Dieke and Crosswhite[11] and the radial integral $(nl|r|n'l')$ for Pr^{3+} and Tm^{3+} can be found in the paper of Rajnak.[12]

For the above-mentioned ions it is consequently straightforward to calculate, within the framework of our approximations, absolute cross sections of Rayleigh scattering of the ground state and electronic Raman scattering from the ground to the first excited states. The results of these calculations are given in Table I.

For the other rare-earth ions the radial wave functions for the $5d$ orbitals are unknown, making it impossible to calculate absolute cross sections. It is possible, however,

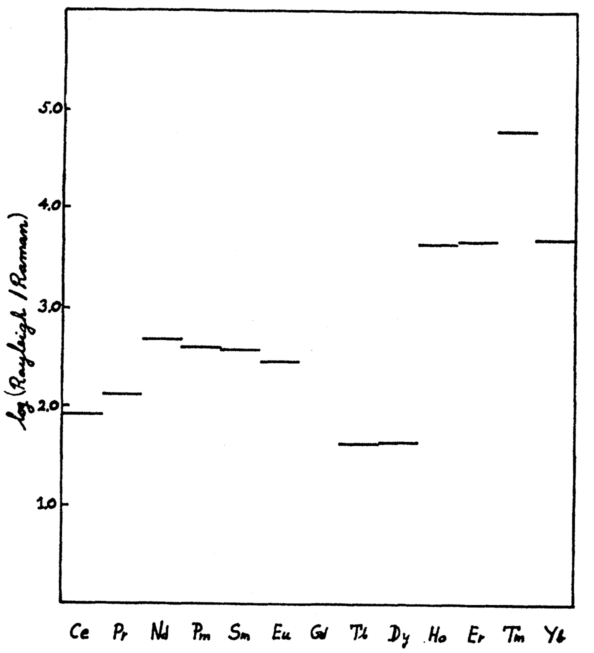

FIG. 1. The Rayleigh-Raman ratio for free trivalent rare-earth ions. The Raman transitions take place between ground and first excited state. The base of the logarithms is 10.

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[9] C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n, d^n and f^n Configurations* (The M.I.T. Press, Cambridge, Mass., 1963).

[10] See Ref. 6 for a detailed discussion of this point.

[11] G. H. Dieke and H. M. Crosswhite, Appl. Opt. 2, 675 (1963).

[12] K. Rajnak, J. Chem. Phys. 37, 2440 (1962).

to calculate the Rayleigh-to-Raman ratio since, in first approximation, that will be independent of the radial wave functions. This ratio has been calculated for Raman transitions between the ground state and first excited state and is shown in Fig. 1.

IV. DISCUSSION

It is of interest to compare the above values of the cross sections for electronic Raman scattering to the values of the corresponding values for vibrational scattering. At present *a priori* calculations similar to these reported here do not exist for vibrational Raman scattering, but experimental data are available. Measurement of absolute Raman cross sections have been performed by Bernstein and co-workers and the ratio of Rayleigh-to-Raman scattering of CCl_4 has been reported by Brandmüller and Schrötter.[13] Unfortunately, their results are not directly comparable to our calculations since these experiments were done using the 4358 Å mercury excitation line, and the scattering tensor, as is well known, is dependent on the frequency of the primary radiation.

Recently, Damen, Leite, and Porto[14] reported on absolute cross sections for Raman scattering of benzene excited with the 6328 Å He-Ne cw gas laser. For the very intense line corresponding to the ν_1 vibration of frequency 992 cm^{-1} they found $\bar{Q}_{\mathrm{Raman}}=0.56\times10^{-28}$ cm^2 and a Rayleigh-to-Raman ratio of 220. As Table I shows, the Rayleigh-to-Raman ratio for electronic scattering of Pr^{3+} is of the same order of magnitude but both scattering processes are down by three orders of magnitude as compared to benzene. This trend is even more pronounced for the case of Tm^{3+} that also illustrates the extreme dependence of the intensity of electronic Raman scattering with the details of the electronic structure of the trivalent lanthanides. This is perhaps even better demonstrated in Fig. 1.

It seems worthwhile to point out that the scattering tensor for electronic Raman transitions is in general asymmetric in contrast to what is the case for most other scattering processes. The degree of antisymmetry is again a highly specific function of the electronic wave functions involved in the transition as has been shown in a previous paper from this laboratory.[6]

APPENDIX

In order to perform the averaging procedure, it is convenient to go from a Cartesian to a spherical basis. In accordance with Edmonds,[8] we define the circular components of the position vector **r** as

$$r_0=z,\qquad r_\pm=\mp(1/\sqrt{2})(x+iy). \tag{A1}$$

The nine components of the reducible spherical tensor $\alpha_{\lambda\mu}$ are then given by

$$(\alpha_{\lambda\mu})_{kn}=\frac{1}{h}\sum_s\frac{\langle\psi_n|r_\lambda|\psi_s\rangle\langle\psi_s|r_\mu|\psi_k\rangle}{\nu_{rk}-\nu}+\frac{[\lambda\rightarrow\mu]}{\nu_{rn}+\nu}. \tag{A2}$$

It is well known that this reducible tensor may be decomposed into a sum of three irreducible tensors of rank 0, 1, and 2, respectively. Denoting the irreducible tensor components as $\alpha_Q{}^K$ [Edmonds,[8] Eq. (5.1.5)],

$$\begin{aligned}\alpha_Q{}^K&=\sum_{\lambda\mu}\alpha_{\lambda\mu}(1\lambda1\mu|11KQ)\\&=\sum_{\lambda\mu}\alpha_{\lambda\mu}(-1)^Q\begin{pmatrix}1&1&K\\\lambda&\mu&-Q\end{pmatrix}(2K+1)^{1/2}.\end{aligned} \tag{A3}$$

The connection between the irreducible tensor components and the usual Cartesian ones is collected below.

$$\begin{aligned}\alpha_0{}^0&=-(1/\sqrt{3})(\alpha_{xx}+\alpha_{yy}+\alpha_{zz}),\\\alpha_1{}^1&=\tfrac{1}{2}(-\alpha_{xz}+\alpha_{zx}-i\alpha_{yz}+i\alpha_{zy}),\\\alpha_0{}^1&=(1/\sqrt{2})(i\alpha_{xy}-i\alpha_{yx}),\\\alpha_{-1}{}^1&=-\tfrac{1}{2}(\alpha_{xz}-\alpha_{zx}-i\alpha_{yz}+i\alpha_{zy}),\\\alpha_2{}^2&=\tfrac{1}{2}(\alpha_{xx}-\alpha_{yy}+i\alpha_{xy}+i\alpha_{yx}),\\\alpha_1{}^2&=-\tfrac{1}{2}(\alpha_{xz}+\alpha_{zx}+i\alpha_{yz}+i\alpha_{zy}),\\\alpha_0{}^2&=(1/\sqrt{6})(2\alpha_{zz}-\alpha_{xx}-\alpha_{yy}),\\\alpha_{-1}{}^2&=\tfrac{1}{2}(\alpha_{xz}+\alpha_{zx}-i\alpha_{yz}-i\alpha_{zy}),\\\alpha_{-2}{}^2&=\tfrac{1}{2}(\alpha_{xx}-\alpha_{yy}-i\alpha_{xy}-i\alpha_{yx}).\end{aligned}$$

It should be noted that this transformation is unitary. Consequently, we have

$$\begin{aligned}|(\alpha_{\rho\sigma})|^2=&\Big(\sum_K\sum_g W_{\rho\sigma}{}^{Kg}\alpha_g{}^K\Big)\\&\times\Big(\sum_{K'}\sum_{g'}W_{\rho\sigma}{}^{K'g'}\alpha_{g'}{}^{K'}\Big)^*,\end{aligned} \tag{A4}$$

where $W_{\rho\sigma}{}^{Kg}$ is the unitary matrix linking the Cartesian basis set with the irreducible spherical basis set. The space-fixed $\alpha_g{}^K$'s must now be expressed in terms of $\alpha_Q{}^K$'s which are defined in relation to a coordinate system fixed in the scattering system. If the Euler angles relating one system to the other are called α, β, and γ, we have [Edmonds,[8] Eq. (5.2.1)]

$$\alpha_g{}^K=\sum_Q\alpha_Q{}^K D_{Qg}{}^K(\alpha,\beta,\gamma). \tag{A5}$$

When Eq (A5) is substituted in Eq. (A4), the averaging over the angles α, β and γ reduces to an averaging of products of the type $D_{Qg}{}^K D_{Q'g'}{}^{K'*}$. Since

$$\int_{\alpha=0}^{2\pi}\int_{\beta=0}^{\pi}\int_{\gamma=0}^{2\pi}D_{Qg}{}^K D_{Q'g'}{}^{K'*}d\alpha\,\sin\beta d\beta d\gamma\Big/$$

$$\int_{\alpha=0}^{2\pi}\int_{\beta=0}^{\pi}\int_{\gamma=0}^{2\pi}d\alpha\,\sin\beta d\beta d\gamma=\delta_K{}^{K'}\delta_Q{}^{Q'}\delta_g{}^{g'}\frac{1}{2K+1} \tag{A6}$$

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[13] J. Brandmüller and H. Schrötter, Z. Physik **149**, 131 (1957).

[14] T. C. Damen, R. C. C. Leite, and S. P. S. Porto, Phys. Rev. Letters **14**, 9 (1965).

[Edmonds,[8] Eq. (4.6.1)], we have

$$|\alpha_{\rho\sigma}|^2=\sum_K\sum_Q\sum_g|W_{\rho\sigma}{}^{Kg}|^2\frac{1}{2K+1}|\alpha_Q{}^K|^2. \quad \text{(A7)}$$

Defining

$$c_{\rho\sigma}{}^K=\sum_g|W_{\rho\sigma}{}^{Kg}|^2$$

we arrive at

$$|\alpha_{\rho\sigma}|^2=\sum_K\sum_Q c_{\rho\sigma}{}^K\frac{1}{2K+1}|\alpha_Q{}^K|^2.$$

The coefficients $c_{\rho\sigma}{}^K$ are easily formed from (A4) to be

	K		
$c_{\rho\sigma}{}^K$	0	1	2
$\rho=\sigma$	$\frac{1}{3}$	0	$\frac{2}{3}$
$\rho\neq\sigma$	0	$\frac{1}{2}$	$\frac{1}{2}$.

It is perhaps worthwhile to point out that the averaging performed above is valid for all random systems independent of their specific nature.

Also the above expressions give directly the depolarization ratio for linearly polarized as well as natural light. The results obtained are of course in agreement with the classical derivations of Placzek,[7] but the present treatment is considerably simpler and more closely related to the scope of the electronic Raman effect.

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Orthogonal Channel Projections in High-Energy Ion-Atom Collisions with Electron Exchanges*

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Approximately orthogonal channel projection operators are constructed for the charge-exchange processes in ion-atom collisions at high energies. The adiabatically perturbed stationary-state wave functions are suitably modified to take into account the motion of the heavy cores to which electrons are bound. By proper adjustment of the phase factors, it is shown that the orthogonality property between states in the modified set can be maintained. The resulting projection operators are mutually *orthogonal everywhere* in the configuration space, and satisfy the asymptotic requirements to first order in the electron-ion mass ratio. Single asymmetric and symmetric charge exchanges as well as double exchanges are studied in some detail, but no actual applications are given.

I. INTRODUCTION

Much interest has been directed both experimentally and theoretically to charge-exchange reactions at high energies involving ions and atoms,[1,2] such as H+H, H+He, He+He, etc. The complexity of the colliding systems is enormous in most cases and the theoretical analysis usually requires many crude approximations. Although some of these approximations may be justifiable under certain conditions, it is often difficult to assess the validity of the simplifications even when they agree with experiments.

Some of the theoretical difficulties are due to our inability to handle the many-particle problems except in an approximate way, but, in the rearrangement collisions, the nonorthogonality between the channels with different cluster compositions gives rise to further complications. Therefore, as a first step toward a more systematic treatment of the charge-exchange processes in the ion-atom collisions, we study, in this paper, the construction of the approximately orthogonal channel projection operators. Construction of such operators is of interest in itself, since, although several methods have been proposed previously,[3–5] *none* of them actually gives the mutually orthogonal operators among the directly coupled rearrangement channels except in the asymptotic regions, where all methods give the same result.

The collisions involving ions and atoms are slow and nearly adiabatic, despite the fact that the typical kinetic energies of interest may be large compared to the characteristic ionization energies. Therefore, the adiabatically distorted electronic wave functions, or the perturbed stationary-state (PSS) wave functions, as

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