NOTIZEN

On the Selection Rules for the Raman Effect

J. Behringer, J. Brandmüller, K. Klauss, and G. Strey
Sektion Physik der Universität München

(Z. Naturforsch. **23 a**, 2121—2122 [1968]; received 21 October 1968)

The selection rules for the Raman effect of Ting are disproved.

In a recently published paper Ting[1] formulated new selection rules for Raman scattering. Among his results are the following statements:

1. When the Born-Oppenheimer approximation is strictly applicable only totally symmetric vibrations are allowed in Raman spectra (p. 1183).
2. Non-totally symmetric vibrations appear in Raman spectra only because of vibronic interactions between the excited states of the molecule due to intramolecular or, with more importance, intermolecular interactions (p. 1183).

It seems to us that these conclusions are neither theoretically nor experimentally justified.

The starting-point of Ting's theoretical arguments is the polarizability tensor element (in Ting's notation, cf. Placzek[2], p. 224)

$$(\alpha_{\varrho\sigma})_i{}^j = \frac{1}{h} \sum_{n,k} \left[\frac{\langle O\, j \,|\, \boldsymbol{e}_\varrho \cdot \boldsymbol{M} \,|\, n\, k \rangle \langle n\, k \,|\, \boldsymbol{e}_\sigma \cdot \boldsymbol{M} \,|\, O\, i \rangle}{\nu_{nk} - \nu_{0j} - \nu} + \frac{\langle O\, j \,|\, \boldsymbol{e}_\sigma \cdot \boldsymbol{M} \,|\, n\, k \rangle \langle n\, k \,|\, \boldsymbol{e}_\varrho \cdot \boldsymbol{M} \,|\, O\, i \rangle}{\nu_{nk} - \nu_{0i} + \nu} \right].$$

Here ϱ, σ represent the Cartesian cordinates x, y, z; i, j, k are the vibrational quantum numbers of the initial, final, and intermediate states; O, n are the electronic quantum numbers of the ground state and an excited electronic state; ν_{0i}, ν_{0j}, ν_{nk}, ν are the energies, devided by Planck's constant h, of the states $|\, O\, i \rangle$, $|\, O\, j \rangle$, $|\, n\, k \rangle$ and of the exciting light.

Now Ting transforms the matrix elements of the electric dipole moment operator in the above expression as follows [p. 1180, Eq. (4)]:

$$\langle n\, k \,|\, \boldsymbol{e}_\varrho \cdot \boldsymbol{M} \,|\, O\, i \rangle = M_{n0}{}^\varrho \langle n\, k \,|\, O\, i \rangle$$

where

$$M_{n0}{}^\varrho = \langle n \,|\, \boldsymbol{e}^\varrho \cdot \boldsymbol{M} \,|\, O \rangle\,.$$

The first of these equations is only correct if $M_{n0}{}^\varrho$ does not depend on the nuclear coordinates. But this is not the case in general because of the following reason: The transition moment $M_{n0}{}^\varrho$ implicitly contains the electronic wave functions which parametrically depend on the nuclear positions. This dependence is still retained in $M_{n0}{}^\varrho$ itself, for the integration leading from $\boldsymbol{e}_\varrho \cdot \boldsymbol{M}$ to $M_{n0}{}^\varrho$ goes only over the electronic position coordinates. In order to show this more clearly let χ be the total internal molecular wave function (after elimination of the translational motion), φ the electronic wave function and u the wave function of the nuclear motions (vibrations and rotations). Then, if the Born-Oppenheimer approximation is applicable, one may separate in case of a non-degenerate state $|\, n\, k \rangle$:

$$\chi_{nk}(\xi, X) = \varphi_n(\xi, X)\, u_{nk}(X)\,. \tag{1}$$

Here ξ represents the totality of all internal electronic position coordinates and X of all internal nuclear position coordinates.

Abbreviating $M_\varrho \equiv \boldsymbol{e}_\varrho \cdot \boldsymbol{M}$ we get explicitly

$$M_{n0}{}^\varrho \equiv \langle n \,|\, \boldsymbol{e}_\varrho \cdot \boldsymbol{M} \,|\, O \rangle = \int \varphi_n{}^*(\xi, X)\, M_\varrho\, \varphi_0(\xi, X)\, \mathrm{d}\xi\,. \tag{2}$$

The dependence of (2) on the nuclear coordinates is evident. The physical reason for the almost unlimited applicability of the Born-Oppenheimer approximation lies in the fact that the electrons, due to their relatively small mass, almost without inertia follow the nuclear motions, so that the electronic wave functions — as formulated in Eq. (1) — may be considered as depending only parametrically on the nuclear positions and not on the nuclear velocities. It is however in general impossible to neglect this dependence on the nuclear positions.

With Eq. (2) we find explicitly for the transition moment given above:

$$\begin{aligned} \langle n\, k \,|\, \boldsymbol{e}_\varrho \cdot \boldsymbol{M} \,|\, O\, i \rangle &= \iint \chi_{nk}{}^*(\xi, X)\, M_\varrho\, \chi_{0i}(\xi, X)\, \mathrm{d}\xi\, \mathrm{d}X \\ &= \iint \varphi_n{}^*(\xi, X)\, u_{nk}{}^*(X)\, M_\varrho\, \varphi_0(\xi, X)\, u_{0i}(X)\, \mathrm{d}\xi\, \mathrm{d}X \\ &= \iint u_{nk}{}^*(X) \left[\varphi_n{}^*(\xi, X)\, M_\varrho\, \varphi_0(\xi, X)\, \mathrm{d}\xi \right] u_{0i}(X)\, \mathrm{d}X \\ &= \int u_{nk}{}^*(X)\, M_{n0}{}^\varrho(X)\, u_{0i}(X)\, \mathrm{d}X\,. \end{aligned}$$

Evidently $M_{n0}{}^\varrho(X)$ in general may not be extracted from the integral over X. Of course $M_{n0}{}^\varrho(X)$ could be expanded into a Taylor's series with respect to X, which in zeroth approximation would yield a constant term allowing the application of Ting's equation (4). It may be shown however, that light scattering is essentially connected with the higher terms in this expansion (see. e. g. Placzek[2], p. 268). These, in turn, again lead to the wellknown old selection rules of the Raman effect.

For experimental evidence Ting refers to the investigations of Stoicheff[3] on Raman scattering of gases. A careful study of Stoicheff's works however shows that his results in no way support Ting's new selection rule. Ting's affirmation that the non-totally symmetric vibrations observed by Stoicheff were "characterized by the absence of Q-branch in rotational structures" (p. 1183) is simply fictitious. Even in spherical tops like CH_4, CD_4, CCl_4, the totally symmetric bands of which

---

[1] C. H. Ting, Spectrochim. Acta **24** A, 1177 [1968].

[2] G. Placzek, Handbuch der Radiologie Bd. VI/2, Akad. Verlagsges. Leipzig 1934, pp. 205—374.

consist *only* of a Q-branch, non-totally symmetric Raman bands with distinct Q-branches were observed (see Stoicheff[3], p. 140 f.; Holzer[4], Holzer and Moser[5]). However even if the Q-branch in the rotational structure of non-totally symmetric Raman bands would be generally missing (which actually is not at all the case) this hardly could be considered as a logically consistent argument for the non-totally symmetric vibrations to be forbidden in the Raman effect. The well-known fact that the totally symmetric lines in the Raman spectrum usually have the highest relative intensities has to be explained in another way (see [6], p. 108). If non-totally symmetric vibrations would appear in the Raman spectrum only because of intermolecular interactions, the intensity ratio of non-totally to totally symmetric lines ought to increase when changing from the gaseous to the liquid state. However the contrary was observed (see e. g. Perzl and Moser[7], Table 1 and 2; Holzer[8]).

---

[3] B. P. Stoicheff, Advances in Spectroscopy (Edited by H. W. Thompson), Vol. 1, Interscience 1964, pp. 91–174.

[4] W. Holzer, Diplomarbeit, Munich 1964.

[5] W. Holzer and H. Moser, J. Mol. Spectr. **13**, 430 [1964].

[6] J. Behringer, Theorie der molekularen Lichtstreuung, Sektion Physik d. Universität München, Lehrstuhl Prof. Brandmüller, 1967.

[7] F. Perzl and H. Moser, J. Mol. Spectr. **26**, 237 [1968].

[8] W. Holzer, Dissertation (Thesis), Munich 1967.

Range of Validity of Static Potential Approximation in Low-Energy Electron Scattering Checked by Cross Section Measurements of Hg between 25 and 150 eV

W. Eitel, K. Jost *, and J. Kessler

Physikalisches Institut, Universität Karlsruhe

(Z. Naturforsch. **23 a**, 2122—2123 [1968]; received 10 October 1968)

A renewed interest in low-energy electron scattering has become evident in the past few years. One of the problems under discussion is: In which energy range can those theories[1–3] be regarded reliable which make the simplifying assumption that scattering takes place in the static (relativistic Hartree) potential of the atom.

Schonfelder[4] had claimed that for mercury this approximation is no longer valid for energies below 500 eV. The present authors[5, 6] showed, however, that this limit is too high, since between 500 and 100 eV there is very good agreement between theoretical predictions and experimental results. The differential cross sections communicated in the present paper display the transition from the energy range where the theories still hold to the energy range where they break down.

The experimental procedure for obtaining these cross sections has been described earlier[6, 7] and can be summarized as follows: An electron beam crosses a mercury atomic beam by which some of the electrons are scattered. The density of the atomic beam is made low enough so that single scattering is ensured[7]. By rotating the electron gun, the scattering angle is varied continuously. The angular resolution for the present measurement is about ±2°. The scattered beam first passes through an energy filter lens which removes inelastically scattered electrons. Then the beam enters a Faraday cup and, after amplification, the intensity I versus scattering angle Θ is recorded by an XY-recorder.

From these measurements the relative cross sections $d\sigma/d\Omega$ were obtained by multiplying the scattered intensity I by $\sin\Theta$, since the effective path length of the

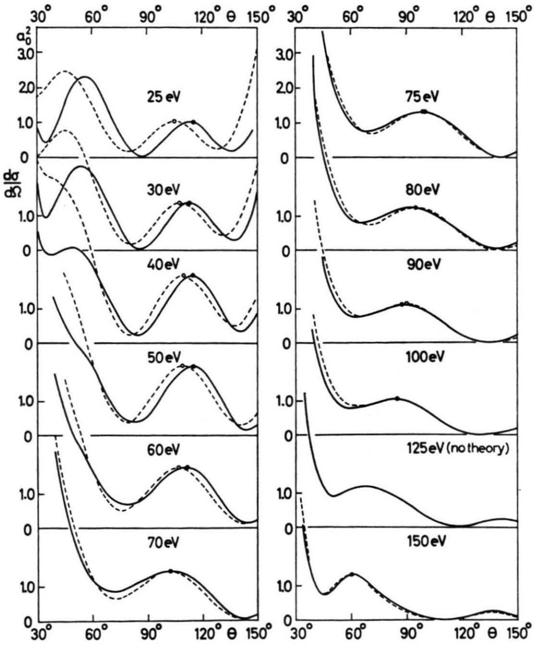

Fig. 1. Differential cross sections for elastic electron scattering by mercury between 150 and 25 eV. Solid line, experiment, dashed line, theory of Coulthard and Walker. At the points marked by a circle, the ordinate of each experimental curve has been normalized to the corresponding theoretical one (a_0 = Bohr radius in hydrogen).

---

* Present address: Stanford University, Stanford, California.

[1] G. Holzwarth and H. J. Meister, Nucl. Phys. **59**, 56 [1964].

[2] P. J. Bunyan and J. L. Schonfelder, Proc. Phys. Soc. London **85**, 455 [1965].

[3] D. W. Walker, Phys. Rev. Letters **20**, 827 [1968].

[4] J. L. Schonfelder, Proc. Phys. Soc. London **87**, 163 [1965].

[5] W. Eitel, K. Jost, and J. Kessler, Phys. Rev. **159**, 47 [1967].

[6] K. Jost and J. Kessler, Z. Physik **195**, 1 [1966].

[7] W. Eitel, K. Jost, and J. Kessler, Z. Physik **209**, 348 [1968].