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Experimental distinction of electric and magnetic transition moments

David M. Jonas,^{a)} Stephani Ann B. Solina,^{b)} R. W. Field, and R. J. Silbey Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Vibronic electric and magnetic dipole transitions have the same rotational structure and relative intensity patterns, so that rotational band structure cannot distinguish parallel electric and magnetic dipole transitions.¹ The point group symmetry of parallel electric and magnetic dipoles is different under all S_n rotation-reflection operators, so that the change in symmetry deduced from the rotational band structure on the two hypotheses may differ. Since fully allowed magnetic dipole transitions are roughly a factor of $(v/c)^2$ less intense than fully allowed electric dipole transitions, (where v is the speed of the charges and c is the speed of light),² sufficiently strong transitions (oscillator strength $f > 10^{-5}$) must be electric-dipole transitions. However, Van Vleck³ has pointed out that electric-dipole transitions between most valence states are forbidden for separated atoms since they correspond to parity forbidden transitions between atomic states with the same electron configuration, while magnetic dipole transitions between valence states are allowed in the separated atom limit. Given the sensitivity of many laser-based spectroscopic techniques and the fact that weak electric dipole transitions are the rule rather than the exception in molecular electronic spectroscopy, it seems worthwhile to have experimental methods for distinguishing weak multipole transitions in general.

It is well known that the only difference in the radiation fields produced by parallel electric and magnetic multipoles of the same order is in their polarizations, which are orthogonal.⁴ In atomic spectroscopy, it is known that either the Zeeman effect in gases⁵ or the polarization dependence of wide angle fluorescence interference in condensed matter⁶ can be used to distinguish among electric-dipole, magnetic-dipole, electric-quadrupole, enforced-dipole transitions caused by electric fields or collisions, etc. Simultaneous polarization and angular correlation measurements have been used to determine the multipole order and type in nuclear cascade transitions.⁷ This note shows that in molecular gases, rotationally resolved double resonance using polarized light can determine the type (magnetic or electric) of one multipole transition if the type of the other transition in the double resonance scheme is known. Stark and Zeeman effects are valuable special cases of the general method proposed here, since the type of a Stark (or Zeeman) transition moment is known a priori to be electric (or magnetic) dipole. It is possible that other variants of this method have been proposed elsewhere.

Parallel electric and magnetic multipoles of the same order constitute tensorial sets of the same degree, so that the rotational parts of the respective transition matrix elements are proportional to each other by the WignerEckart theorem.⁸ Electric multipole matrix elements may thus be used to calculate the rotational intensity factors for a parallel magnetic multipole transition as long as it is kept in mind that H is perpendicular to E for an electromagnetic wave. For linearly polarized light, the M_J sublevel distribution produced by a magnetic multipole transition is the same as the M_J distribution produced by an electric-multipole transition of the same order with perpendicularly polarized light. This is the basis for distinguishing magnetic from electric dipole transitions using the Zeeman effect in atomic spectroscopy.⁹ We note here that if the $|M_J|$ dependence of the Stark shifts is detectable (e.g., first-order Stark effect), the Stark effect can also distinguish between electric and magnetic transition moments.

For linearly polarized light propagating in the laboratory x direction with E parallel to z, one uses the factor ϕ_z in the direction cosine matrix elements of Townes and Schawlow¹⁰ for an electric-dipole transition. Since H is parallel to y, the appropriate factor for a magnetic-dipole transition is proportional to ϕ_y . Inspection of these factors shows that for electric-dipole transitions, the P and R branches preferentially populate low $|M_J|$ sublevels and the Q branch preferentially populates high $|M_J|$ sublevels. For magnetic dipole transitions the roles of the P,R vs Q branches are reversed: The P and R branches preferentially populate high $|M_J|$ sublevels and the Q branch preferentially populates low $|M_J|$ sublevels.

As a specific example we consider the first-order Stark effect on a perpendicular ($\Delta K = \pm 1$) vibronic transition in a prolate symmetric top. If the static electric field is oriented along z, the level $|J,K,M_J\rangle$ experiences a firstorder Stark shift $V_{\text{STARK}} = \mu E K M_J / J (J+1)$, where μ is the permanent electric-dipole moment. For transitions from K = 0 in the ground state to K = 1 in the excited state, the splitting of a given line will be determined by the first-order Stark effect in the excited state. For light polarized parallel to the static electric field along z, electricdipole Q-branch transitions will have greatest intensity for the high $|M_I|$ components which have the largest Stark shifts, while electric-dipole P and R branches will have greatest intensity for low $|M_{I}|$ components which have the smallest Stark shifts. If the fields are insufficient to resolve all the $|M_j|$ components, the Q-branch transitions will split into doublets while the P- and R-branch lines will only broaden slightly. However, for magnetic dipole transitions, the P and R branches will split and the Q branch will broaden!

Observation of the Stark splitting pattern in the *b*-dipole $\widetilde{A} \leftarrow \widetilde{X} 4_1^0$ band of the near prolate top formaldehyde¹¹ experimentally proves an electric-dipole transition type for

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this band, as do Stark quantum beat studies on both H₂CO and D₂CO.¹² The intensity pattern of the fully resolved M_J components in the *c*-dipole infrared v_4 band of D₂CO (Ref. 13) proves the electric-dipole character of this transition. Taken together, the observations on D₂CO experimentally prove that the \tilde{A} state of formaldehyde has electronic symmetry A_2 , confirming Innes assignment of the *a*-dipole $\tilde{A} \leftarrow \tilde{X}$ origin band as a magnetic dipole transition. The Stark effect on the $\tilde{A} \leftarrow \tilde{X} 4_0^2$ magnetic-dipole transition in formaldehyde should show an anomalous Stark effect: For light polarized parallel to the static electric field the Qbranches will broaden while the P and R branches will split.

More generally, rotational intensity patterns in double resonance spectra can be used to determine the type of one dipole transition if the electric vs magnetic type of the other is known. For simplicity, we assume that the M_{I} distribution in the initial state is isotropic (equal population in all M_I sublevels). According to the considerations above, polarized light in the first step of double resonance creates unequal population in the M_I sublevels. If both dipole transitions in double resonance are of the same type, one expects sequential double resonance transitions of the types QQ, RR, RP, PR, and PP will be more intense for both excitation sources polarized parallel than perpendicular, while sequential double resonance transitions of the types QR, QP, PQ, and RQ will be more intense for perpendicular than parallel polarizations. This expectation may be verified by examining the sign of the expressions for either the "degree of polarization," P, or "polarization anisotropy," R, for electric-dipole resonance fluorescence.¹⁵ Double resonance with one magnetic-dipole transition and one electric-dipole transition will reverse the situation: QQ_{i} RR, RP, PR, and PP will be more intense for perpendicular polarization of the two excitation sources and OR, OP, PO and RQ will be more intense for parallel polarization.

Experimentally, rotating the polarization without affecting the spatial overlap of the two beams in a double resonance experiment may be difficult. In practice, it may often be easier to compare the relative intensities of P, Q, and R lines in a parallel polarization double resonance spectrum to those in a perpendicular double resonance spectrum recorded via the same pump transition. A comparison is important since it is possible for perturbations (e.g., Coriolis) to affect only the levels reached by the Qbranch (or the P and R branches). Such comparisons may be useful in separating electric and magnetic dipole transitions in the Coriolis perturbed SEP spectrum of formaldehyde. More generally, the comparisons suggested here can experimentally determine the change in symmetry of a dipole transition in double resonance.

It is notable that the double resonance technique for distinguishing electric and magnetic dipole transitions is applicable even to singlet Σ electronic states of centrosymmetric molecules composed of spin zero nuclei, which have no Stark or Zeeman effects, no pure rotational spectra, and

no nuclear magnetic resonance (NMR) spectrum.¹⁶ As long as a transition can be linked by double resonance to a transition which is too strong to be a magnetic-dipole transition (e.g., Rydberg transition) or to a transition with a theoretically known change of symmetry, the second transition type can be determined by rotationally resolved double resonance with polarized light. The techniques outlined here should be useful for determining the change of symmetry in transitions among electronic states for which accurate ab initio calculations are not available. Magneticdipole electronic transitions should be especially strong and abundant in molecules containing atoms with strong magnetic-dipole transitions (e.g., oxygen, transition metals). Infrared vibrational circular dichroism in chiral molecules,¹⁷ which requires a mixed multipole moment derivative, makes the apparent complete absence of pure magnetic-dipole vibrational transitions in achiral molecules suspicious-extremely weak vibrational magnetic-dipole transitions between states differing by the symmetry of a rotation should be observable in some molecules by modern infrared techniques. For instance, the π_g bending fundamentals of linear YXXY molecules should be infrared magnetic dipole active if the XY bond is polar so that the vibrational angular momentum produces a magnetic moment. It is hoped that the methods outlined here will be generally useful to spectroscopists.

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^{a)}AT&T Bell Labs Doctoral Scholar.

- ^{b)}NSF Predoctoral Fellow.
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