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Laser-absorption profiles of the magnesium–rare-gas ($3s\ {}^1\Sigma^+$–$4s\ {}^1\Sigma^+$) molecular bands

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We have measured the absorption profiles of the Mg–rare-gas ($3s\ {}^1\Sigma^+$–$4s\ {}^1\Sigma^+$) collision-induced molecular bands. The experimental results for the Mg-He and Mg-Ne profiles are compared with a semiquantitative theoretical model based on model potential curves and an assumed transition dipole-moment function. Reasonably good agreement is obtained supporting our interpretation for the nature of these collision-induced absorption bands.

Collision-induced dipole absorption processes occurring in the far wings of forbidden atomic lines have been observed and investigated for many years.[1–7] The most well studied of these transitions are the low-lying ${}^2\Sigma^+$-${}^2\Sigma^+$ alkali-metal–rare-gas molecular bands correlating with the ${}^2S$-${}^2S$ and ${}^2S$-${}^2D$ forbidden atomic lines.[1–4] The experimental and theoretical work of a number of groups[1–7] has led to a reasonable semiquantitative understanding of the origin of these bands as Franck-Condon "quasimolecular" transitions, where the molecular dipole moment is a function of internuclear separation R determined by the collisional mixing of opposite parity states. The bands are thus fundamentally similar to those commonly observed and studied in the far wings of pressure-broadened (allowed) atomic lines and can be analyzed using the well-established formalism of line-broadening theory.[6–9] The detailed band shapes are determined by both the usual quasimolecular difference potentials and by the transition-dipole-moment function that vanishes as $R \rightarrow \infty$.

We have recently reported our studies of the Ca–rare-gas ($4s\ {}^1\Sigma^+$–$5s\ {}^1\Sigma^+$) molecular bands[10] and have compared these observations with previous work on the alkali–rare-gas transitions. Significant differences were noted and qualitatively explained using the model potential curves of Malvern[11] as a basis. In this paper we describe similar studies of the lowest-lying Mg–rare-gas ($3s\ {}^1\Sigma^+$–$4s\ {}^1\Sigma^+$) molecular bands. These results will be compared with the previous measurements in the calcium system,[10] and with semiquantitative theoretical predictions based on the model potential curves of Malvern[11] including an assumed transition-dipole-moment function. Reasonably good agreement is obtained, supporting our basic interpretation for these collision-induced absorption bands.

The experimental method has been described in detail in Ref. 10. A frequency-doubled yttrium aluminum garnet 30-hz Nd:YAG laser was used to pump a pulsed dye laser operated with Rhodamine 610 laser dye in an oscillator-amplifier arrangement. The tunable output near 580 nm was frequency doubled in an angle-tuned potassium dihydrogen phosphate (KD*P) crystal to the spectral region near 290 nm. This output was then subsequently mixed with the YAG fundamental in a second angle-tuned KD*P crystal to produce tunable laser output near the Mg($3s^2\ {}^1S_0$–$4s\ {}^1S_0$) strictly forbidden line at 230 nm. The unwanted wavelengths were separated with a dichroic mirror and a bandpass filter centered at 230 nm. The laser pulse energy was $\sim 15\ \mu J$ with a pulse length ~ 5 ns. The laser was softly focused ($I_L \sim 200$ kW/cm^2) into a stainless steel oven ($T \sim 750$ K) containing Mg metal vapor ($[\mathrm{Mg}] \sim 10^{14}/\mathrm{cm}^3$) and inert buffer gas at a typical pressure of 700 Torr. The absorption spectrum was measured by monitoring the spectrally and temporally integrated cascade fluorescence on the Mg($3p\ {}^1P_1^0$–$3s^2\ {}^1S_0$) resonance line at 285 nm as a function of laser wavelength.[3] This method is significantly more sensitive than classical white-light absorption techniques. Possible quenching of the laser-excited Mg*($4s\ {}^1S_0$) level through channels other than resonance cascade fluorescence has been demonstrated to be unimportant in similar systems and should not be a problem here.[3,10] The instrumental resolution, determined by the

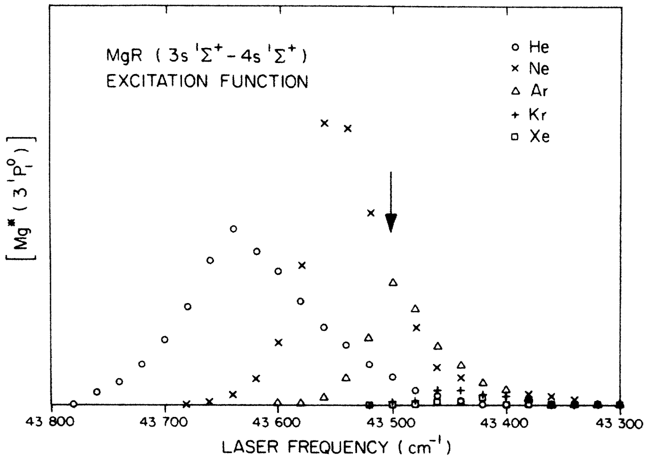

FIG. 1. Absorption profiles for the Mg–rare-gas ($3s\ {}^1\Sigma^+$–$4s\ {}^1\Sigma^+$) molecular bands. The arrow denotes the position of the forbidden atomic transition Mg($3s\ {}^1S_0 \rightarrow 4s\ {}^1S_0$).

laser bandwidth, was ~0.02 nm.

The absorption profiles for the Mg–rare-gas ($3s\ ^1\Sigma^+ - 4s\ ^1\Sigma^+$) transitions are shown in Fig. 1. The location of the forbidden atomic transition ($3s^2\ ^1S_0 \rightarrow 4s\ ^1S_0$) at an energy of 43 503 cm^{-1} is shown with an arrow. It is clear that the strongest molecular bands occur for He, Ne, and Ar, with the Kr and Xe bands being extremely weak. These observed profiles are linear in laser intensity, buffer gas pressure, and Mg density, demonstrating that we are indeed observing single-step molecular absorption. The strong Mg-He and Mg-Ne bands are slightly blue shifted, the weak Mg-Kr and Mg-Xe bands are slightly red shifted, and the Mg-Ar profile is centered about the forbidden transition energy at ~43 500 cm^{-1}. The observations of the relative strengths and shifts of these bands are, again, in stark contrast with previous work on the alkali-metal–rare-gas forbidden transitions[1–3] that generally demonstrate a very strong far-red-wing absorption band. These results, however, are completely consistent with our previous measurements on the analogous Ca–rare-gas ($4s\ ^1\Sigma^+ - 5s\ ^1\Sigma^+$) molecular system,[10] and with the work of Ueda *et al.*[5]

A qualitative interpretation of these observations has been given in Ref. 10 and will not be repeated here. Rather, in Fig. 2 we present a quantitative comparison of the observed Mg-He and Mg-Ne profiles with theoretical predictions. These predictions (the solid curves in Fig. 2) are based on the model potential curves of Malvern,[11] using a single-perturber quantum-mechanical calculation for the line profile and an assumed transition dipole-moment function.

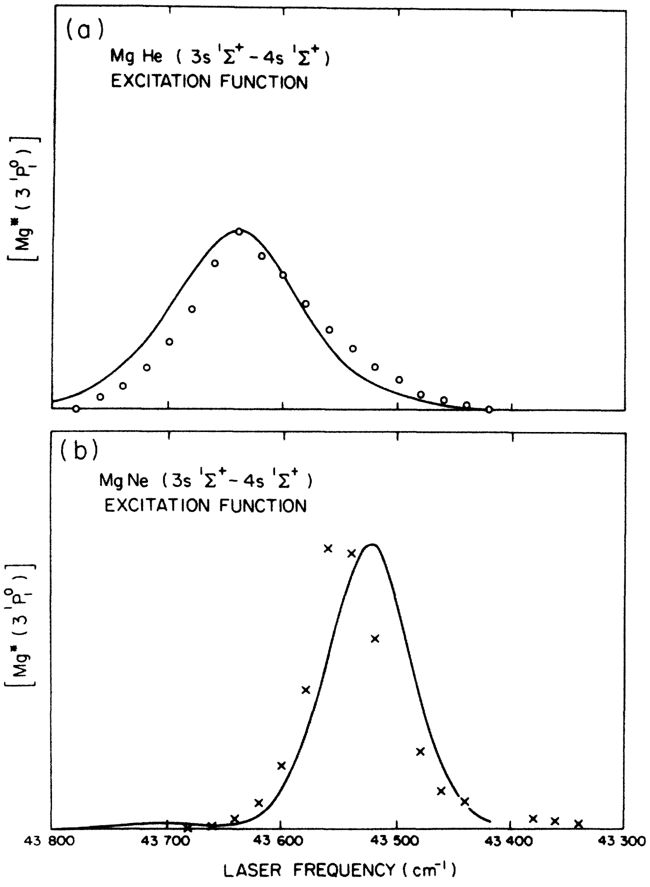

FIG. 2. Comparison of the experimental and theoretical (solid lines) absorption profiles for (a) Mg-He and (b) Mg-Ne.

The quantum-mechanical formulation for the line-profile calculation has been described in detail in Ref. 12. The model potential curves of Malvern[11] have been used to obtain a theoretical excited-state–ground-state difference potential. The ($4s\ ^1\Sigma^+ - 3s\ ^1\Sigma^+$) difference potential was measured as a set of points directly from the published curves. In order to avoid unphysical oscillations in the calculated profile caused by these crude measurements we chose to fit the potential to an analytic form.

The difference potential (for either the helium or neon case) increased slowly as R decreased from ∞ to a maximum at a rather large internuclear distance, and then dropped rapidly at smaller R. In fact, the difference potential showed a qualitative shape that could be nicely approximated by an inverted Morse potential of the form

$$V(R) = D\left(1 - e^{-B(R-R_e)^2}\right) + (E - D)\ .$$

This Morse potential gave a very reasonable fit to the measured difference potential; the fit parameters are specified in Table I. The difference potential maxima, higher for Mg-He than for Mg-Ne, presumably result from an interaction (avoided crossing) between the $4s\ ^1\Sigma^+$ and the lower-lying repulsive $3p\ ^1\Sigma^+$ molecular state. We believe the observed absorption bands arise from intensity enhancement (i.e., classical satellites) associated with these extrema.

We also included in the calculation a crude dipole-moment function of the form

$$D(R) = \begin{cases} 1, & R \le R_c \\ \left[\dfrac{R_c}{R}\right]^7, & R > R_c \end{cases}$$

where R_c is an adjustable parameter. In our picture of the interaction, the transition dipole-moment function is induced by the collisional mixing with the $3p\ ^1\Sigma^+$ molecular state of opposite parity. Therefore we assumed that R_c should roughly correlate with the position of the avoided crossing between the $4s\ ^1\Sigma^+$ and $3p\ ^1\Sigma^+$ repulsive states. While this avoided crossing region is not well localized, it probably occurs near the maximum of the excited-state–ground-state difference potential. Thus we chose the values $R_c = R_e$ in Table I. This model gives a reasonable long-range form[6] as $R \rightarrow \infty$ and assumes that for $R \le R_c$, the molecular state changes character to become essentially of odd parity. It is important to note the

TABLE I. Theoretical model parameters. All quantities are in a.u.

	B	D	E	$R_e (= R_c)$
Mg-He	0.391	-8.46×10^{-4}	0.182	9.3
Mg-Ne	0.486	-7.23×10^{-5}	0.181	8.7

theoretical results are not very sensitive to the value of R_c, nor to its long-range form as long as it falls off rapidly as $R \rightarrow \infty$. In fact, a dipole-moment function that falls off exponentially beyond $R \sim R_c$ gives essentially identical results. The position of the absorption profile maximum is apparently determined predominantly by the difference potential extremum.

Given the approximations in this theoretical model, the fit in Fig. 2 is very good. The remaining discrepancies are probably due primarily to the crude model chosen for the theoretical difference potential. Nevertheless, the agreement clearly indicates that our interpretation of these dipole-collision-induced absorption bands is fundamentally correct.

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[1] M. Lapp, Phys. Lett. **23**, 553 (1966).

[2] A. Tam, G. Moe, W. Park, and W. Happer, Phys. Rev. Lett. **35**, 85 (1975); G. Moe, A. Tam, and W. Happer, Phys. Rev. A **14**, 349 (1976); A. Tam, T. Yabuzaki, S. M. Curry, and W. Happer, *ibid.* **18**, 196 (1978).

[3] B. Sayer, M. Ferray, and J. Lozingot, J. Phys. B **12**, 227 (1979); **13**, 177 (1980); I. Dubourg, M. Ferray, J. P. Visticot, and B. Sayer, *ibid.* **19**, 1165 (1986); I. Dubourg and B. Sayer, *ibid.* **19**, 2291 (1986).

[4] J. Pascale and J. Vandeplanque, J. Chem. Phys. **60**, 2278 (1976); J. Pascale, *ibid.* **67**, 204 (1977).

[5] K. Ueda, T. Fujimoto, and K. Fukuda, J. Phys. Soc. Jpn. **49**, 1147 (1980); **50**, 623 (1980); K. Ueda, Y. Ashizawa, and K. Fukuda, *ibid.* **50**, 1330 (1980); K. Ueda and K. Fukuda, J. Phys. Chem. **86**, 678 (1982).

[6] A. Gallagher and T. Holstein, Phys. Rev. A **16**, 2413 (1977).

[7] G. Alber and J. Cooper, Phys. Rev. A **33**, 3084 (1986).

[8] R. E. M. Hedges, D. L. Drummond, and A. Gallagher, Phys. Rev. A **6**, 1519 (1972).

[9] N. Allard and J. Kielkopf, Rev. Mod. Phys. **54**, 1103 (1982), and references therein.

[10] P. D. Kleiber and K. M. Sando, Phys. Rev. A **35**, 3715 (1987).

[11] A. R. Malvern, J. Phys. B **11**, 831 (1978).

[12] P. S. Herman and K. M. Sando, J. Chem. Phys. **68**, 1153 (1978).