JOINT INSTITUTE FOR LABORATORY ASTROPHYSICS

UNIVERSITY OF COLORADO

REPORT

NATIONAL BUREAU OF STANDARDS

TUNABLE GAS LASERS
UTILIZING GROUND STATE DISSOCIATION

by

A. V. Phelps

JILA REPORT No. 110

University of Colorado
Boulder, Colorado

September 15, 1972

36

The Joint Institute for Laboratory Astrophysics was created in 1962 through the collaboration of the University of Colorado and the National Bureau of Standards, U. S. Dept. of Commerce, for the purpose of furthering research and graduate education in laboratory astrophysics—laboratory and theoretical investigations of physical processes of astrophysical importance. The major fields of activity are low energy atomic physics, theoretical astrophysics, and aerodynamics.

The institute is located on the campus of the University of Colorado. The academic staff are members of the Department of Physics and Astrophysics, of the College of Arts and Sciences, or the Department of Aerospace Engineering Sciences, of the College of Engineering. In addition to certain members of these faculties, the scientific staff of JILA includes Visiting Fellows and Members from other institutes, graduate students and postdoctoral appointees.

The JILA is operated as a partnership between CU and NBS by the Fellows of JILA, responsible through their Chairman to the Director, the NBS, and the President, the University of Colorado. NBS appointed staff members of JILA constitute the NBS Laboratory Astrophysics Division (274.00).

JOINT INSTITUTE FOR LABORATORY ASTROPHYSICS

UNIVERSITY OF COLORADO

REPORT

NATIONAL BUREAU OF STANDARDS

JILA Report #110

TUNABLE GAS LASERS
UTILIZING GROUND STATE DISSOCIATION

by

A. V. Phelps

NOTE: The material contained in this report will not be published in any other form.

University of Colorado
Boulder, Colorado
September 15, 1972

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by U.S. Army Research Office-Durham under Contract No. DAHC04 72 C 0047.

ABSTRACT

Experimental and theoretical studies of the spectral distribution of fluorescence and absorption in the far wings of alkali resonance lines broadened by rare gas atoms will be used as a basis for the prediction of approximate values for the laser gain in such mixtures and in Xe_2, i.e., ground state dissociation lasers. This discussion makes use of the quasistatic theory of spectral line broadening which relates the observed fluorescence intensity to the intermolecular potentials for the bound excited state and the dissociating ground state of the molecule.

I. INTRODUCTION

Recent papers by Bassov and coworkers[1] and by Koehler and coworkers[2] have pointed to the possibility of stimulated emission in the vacuum ultraviolet as the result of excitation of gases such as xenon. This work is an extension of earlier work by Carbone and Litvak[3] in mercury vapor and by Palmer[4] and others in hydrogen. The basic idea of these lasers is that if one forms an excited molecule which then can radiate to a repulsive ground state, one can readily satisfy the conditions for population inversion. In this paper we will refine this condition for population inversion and so derive the condition initially stated by Carbone and Litvak. In addition, we will examine the very important question as to the magnitude of the stimulated emission cross sections expected for such molecular systems.

The quantitative basis of our analysis is an application of the quasi-static theory of spectral line broadening as expressed by Kuhn and others[5] many years ago. We will illustrate the application of this theory using results obtained recently by Hedges, Drummond, and Gallagher[6] for cesium-rare gas systems and by Behmenburg[7] for mercury-argon mixtures. These authors made use of the quasistatic theory to derive potential energy curves for ground state and excited molecules from measurements of fluorescence spectral intensities. We, of course, are primarily interested in predicting fluorescent intensities and stimulated emission cross sections from a knowledge of molecular potential energy curves. Thus, Fig. 1 illustrates a recent calculation of molecular potential energy curves for the hydrogen-helium molecule.[8] We would like to know whether this molecular system is a good candidate for the observation of stimulated emission. We note that

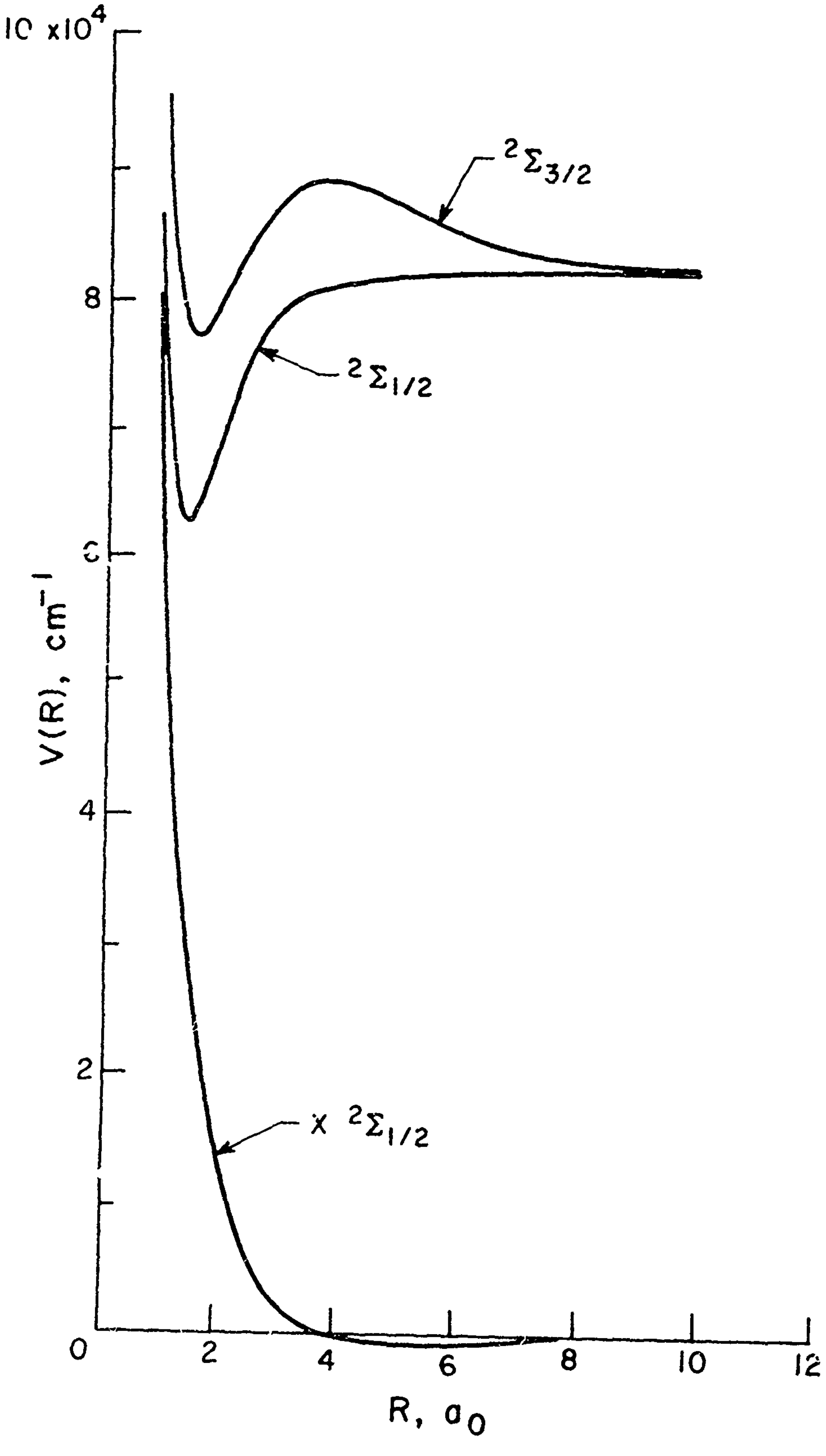

Fig. 1. Theoretical potential energy curves as calculated by Slocomb, Miller and Schaefer (Ref. 8).

the ground state is highly repulsive so that inversion conditions should be readily satisfied. Our question then is, whether or not the stimulated emission cross section is sufficiently large so as to allow a reasonable gain in an attainable discharge? We will also need to consider competing absorption processes.

II. RELATION BETWEEN POTENTIAL CURVES AND SPECTRAL LINE SHAPE

Figure 2 shows potential energy curves, frequency differences, and population factors appropriate to a discussion of the molecular continuum emission based on that of Hedges, Drummond, and Gallagher.[6] The upper pair of curves are potential energy curves such as one might find for the ground state and the first excited state of an alkali rare gas molecule. The excited state is labelled $A^2\Pi_{1/2}$ and the ground $X^2\Sigma_{1/2}$. We are concerned with an atom in an excited state having a total energy E_1 which collides with a rare gas atom in the ground state to form an $A^2\Pi_{1/2}$ molecule. We consider radiation occurring at an internuclear separation between R and $R + \delta R$. According to the classical limit of the Franck-Condon principle, the difference between the total potential energy of the system and the molecular energy curve in the excited state, i.e., the kinetic energy, must be conserved in a radiative transition to the ground state. This results in a departing ground state alkali atom with kinetic energy E_f.

The energy difference between the excited A state and the ground X state is indicated as a function of internuclear separation by the middle curve. We note that for the potential energy curves of this graph there is a unique curve of potential energy difference as a function of internuclear separation. This means that each measurement of the frequency of the radiation corresponds uniquely with a particular internuclear separation. In order to determine the absolute potential energy, one measures the change in intensity with temperature. This change in intensity with temperature is determined by the number of molecules which have the internuclear separation between R and $R + \delta R$ at the time of radiation. Two limiting cases are apparent. The first is a low pressure limit in which

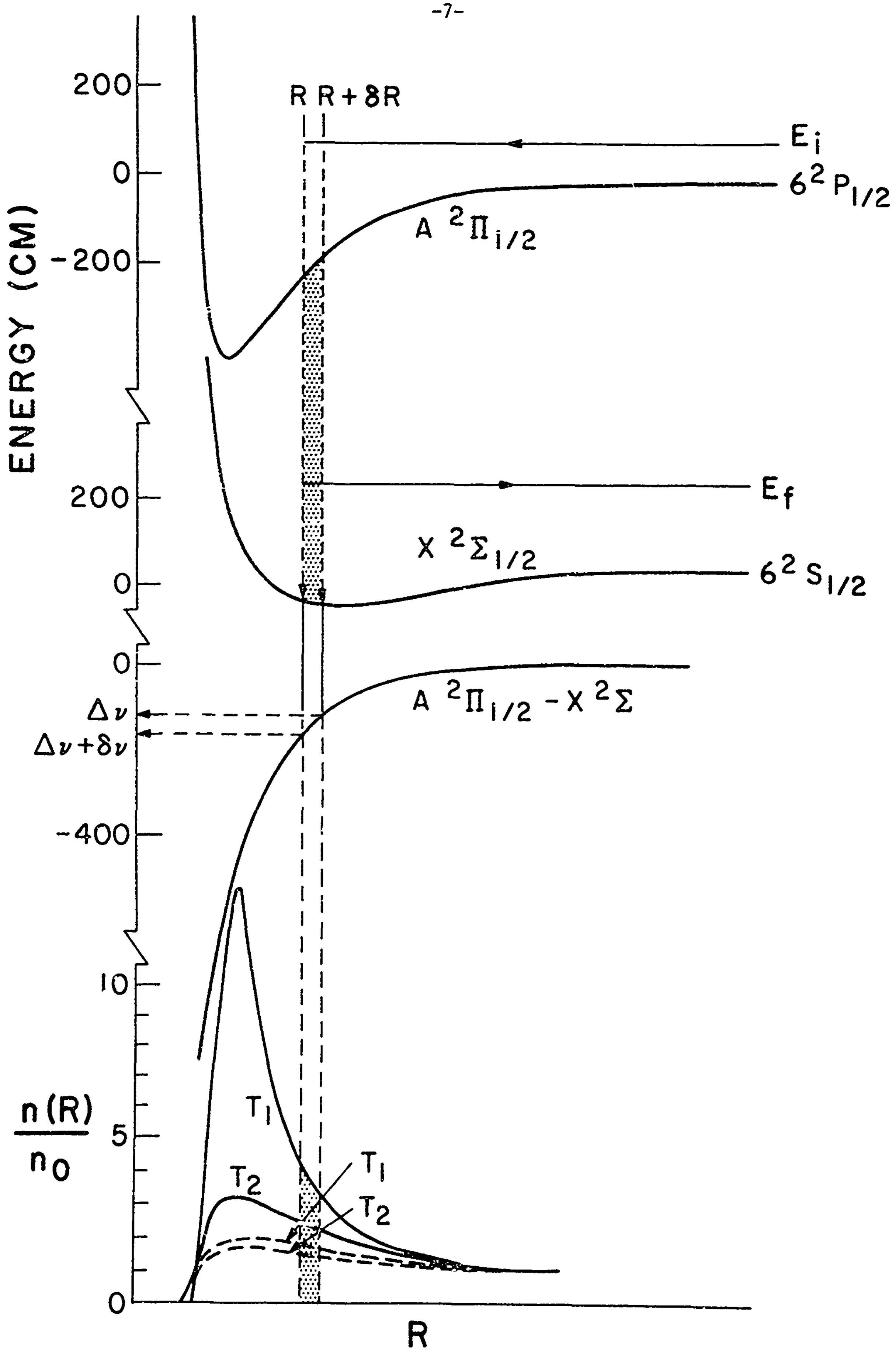

Fig. 2. Diagram for discussion of quasistatic theory of spectral line broadening showing: (a) typical potential energy curves, (b) potential energy differences, and (c) relative densities of perturbers for various temperatures and equilibrium assumptions. From Ref. 6.

the excited atom in the $6^2P_{1/2}$ state with a total energy E_1 collides with the ground state rare gas atom along some trajectory at constant total energy and always has the possibility of escaping from the molecular complex. In this case the number of molecules to be found at a given internuclear separation is relatively independent of temperature as indicated by the dashed curves at the bottom of the figure. At high pressures the unstable excited molecule can readily be collisionally stabilized form bound molecules. In this discussion we will ignore the discrete nature of the vibrational states of the molecule and calculate the relative populations using continuum relations. In this limit, the molecular density is in equilibrium with the density of free excited atoms and one obtains the relative population curves indicated by solid lines at the bottom of the figure. The curve for T_1 is that for a lower temperature than that for T_2 and indicates that many more atoms are to be found in the molecular state at the lower temperature. By varying the gas temperature one can observe the dependence of radiation at a given frequency on temperature and from this determine the binding energy of the excited state corresponding to the observed frequency. One now has the potential energy of the excited state as a function of the observed frequency difference, and can calculate the potential energy of the ground state as a function of the observed frequency difference. In order to determine the relationship between the frequency difference and the internuclear separation, one makes use of the observed magnitude of the intensity of the fluorescence.

An approximate derivation of the theory of quasistatic line broadening is as follows: The relationship between the number of the excited atoms which are in a molecular state capable of radiating at frequency ν, compared to the total number of atoms in the upper state of the atom, can be expressed as

$$\frac{\delta N^{u}(\nu)}{N_u} = 4\pi R^2(\nu)\delta R(\nu) N_o P_j(\nu) . \qquad (1)$$

This fraction is given by the volume element $4R^2\delta R$ times the density of perturbing atoms, N_o, times the population factor P_j. The population factor P_j contains a statistical weight ratio which takes into account the fact that there may be more than one molecular state which can be formed from the excited alkali and the rare gas atoms. It also includes the Boltzmann factor giving the relative population of excited molecules as a function of the potential energy. The fraction of atoms capable of radiation in a frequency $\delta\nu$ is obtained by dividing Eq. (1) by $\delta\nu$ and substituting the appropriate statistical weight factors and the Boltzmann factor to obtain

$$\frac{\delta N^{u}(\nu)}{N_u \delta\nu} = \frac{4\pi R^2(\nu)}{\left.\frac{\delta\nu}{\delta R}\right|_{\nu}} N_o \frac{g_{ju}}{g_{fu}} \exp\left(-\frac{V_u(\nu)}{kT}\right) . \qquad (2)$$

Here g_{ju} and g_{fu} are the statistical weight factors for the j^{th} molecular state formed from the free excited atom with a statistical weight g_{fu} and $\Delta V_u(\nu)$ is the increase in the excited state potential energy from its value at infinite perturber separation to its value at the separation at which the radiated frequency is ν. The fluorescent intensity is obtained by multiplying Eq. (2) by the photon energy $h\nu$ and the Einstein transition probability A which is a function of internuclear separation R,

$$I(\nu) = \frac{h\nu A_{u\ell}(R) R^2(\nu)}{\left.\frac{d\nu}{dR}\right|_{\nu}} N_o N_u \frac{g_{ju}}{g_{fu}} \exp\left(-\frac{V_u(\nu)}{kT}\right) . \qquad (3)$$

Bates[5] and Hedges, Drummond, and Gallagher[6] argue that the Einstein coefficient should vary as the cube of the frequency for hydrogen and for alkali-rare gas systems, respectively. Equation (3) can be rewritten so as to express the radius or internuclear separation as a function of quantities which depend only on frequency. Integration of this equation then gives the cube of the radius as a function of the observed frequency plus an undetermined integration constant. This constant must be determined from auxiliary experiments such as measurements of the internuclear potential of the ground state at some particular radius as determined from molecular beam scattering measurements. Of particular interest to us is the appearance of the quantity $d\nu/dR$ in the denominator of Eq. (3). This means that if the energy difference of the potential curves should become independent of radius with a resultant zero derivative, one obtains a singularity in the fluorescent intensity as a function of frequency. This often occurs and leads to what are called satellites. Of course the singularity is unrealistic and is smoothed out by motional effects not included in this theory.

Figure 3 shows typical fluorescent intensity data obtained by Hedges, Drummond, and Gallagher[6] for the cesium argon system excited with 8521-Å radiation and observed with a very high speed monochrometer. One interesting feature of these data is the variation with temperature of the fluorescent intensity at wavelengths between 8600 and 9200 Å. Here one observes an increase in fluorescent intensity with decreasing temperature corresponding to an increasing population of molecules in the bound excited state of the CsAr molecule. These data are used to determine the depth of the potential well in the excited state. In the blue wing one notes that the intensity increases with increasing temperature. This behavior is characteristic of a repulsive portion of the excited state potential energy curve. The same behavior is observed in the red wing at wavelengths beyond 9200 Å.

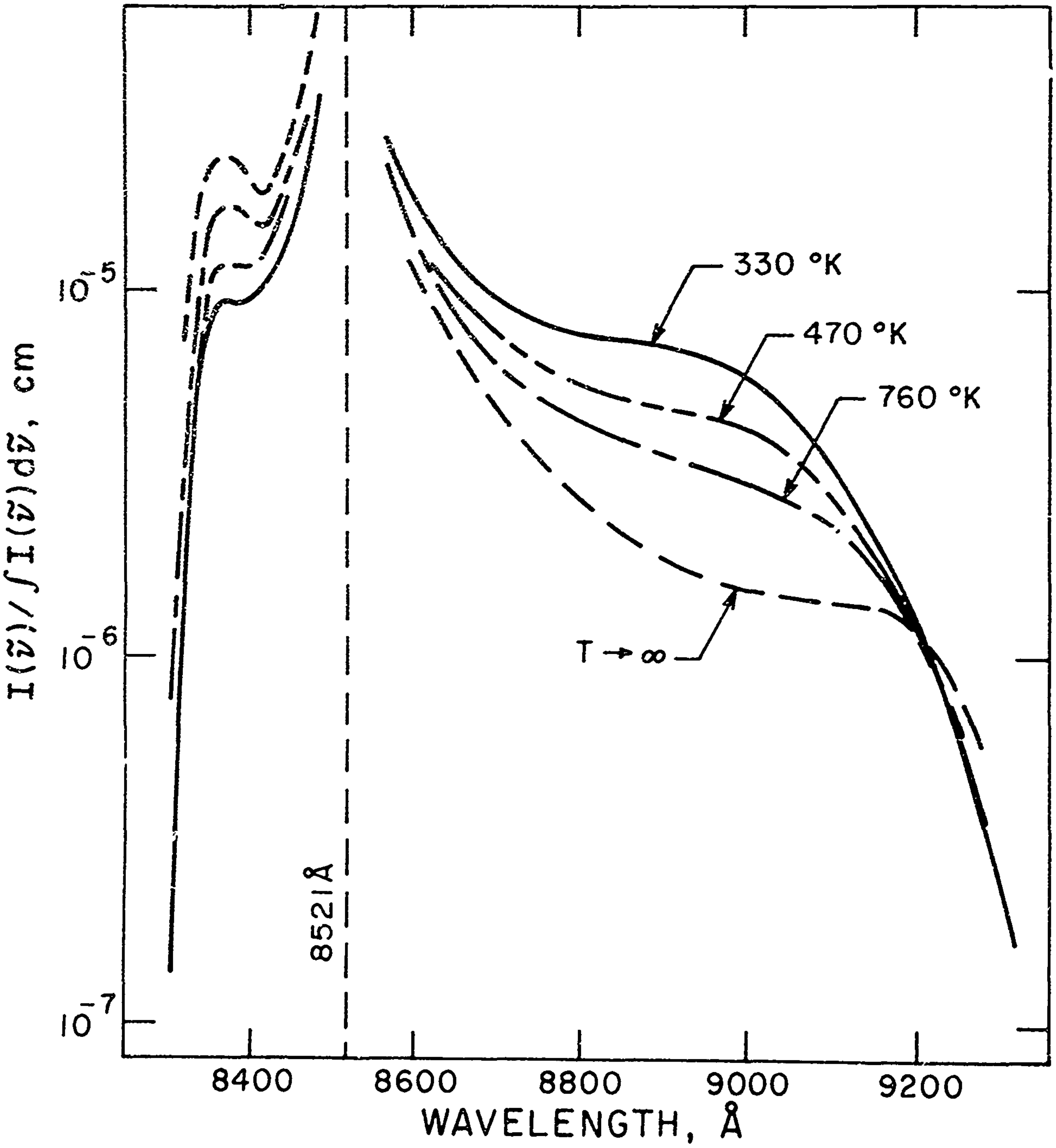

Fig. 3. Normalized fluorescent intensity for Cs excited with 8521 Å and broadened by argon. Data from Ref. 6.

The potential energy curves for this system are shown in Fig. 4. The only available theoretical calculation for this system, i.e. that by Baylis,[6] has shown poorer agreement with these curves as the atomic wavefunctions used in the calculation have been improved. There is some reason[9] to believe that the theory used by Baylis[10] should not be expected to be too accurate for the $\Pi_{3/2}$ and $\Pi_{1/2}$ state of this system.

The second source of data for analyses of this type is the absorption spectra shown in Fig. 5. These data obtained by Chen and Phelps[11] cover the spectral range from about one angstrom to several hundred angstroms from line center. Unfortunately, the quasistatic theory discussed previously is less accurate in the spectral range covered in these experiments. One is therefore very hesitant to construct potential energy curves on the basis of these data. One can, however, use detailed balancing arguments to construct stimulated emission curves directly from the absorption profiles. This is discussed in Sec. III.

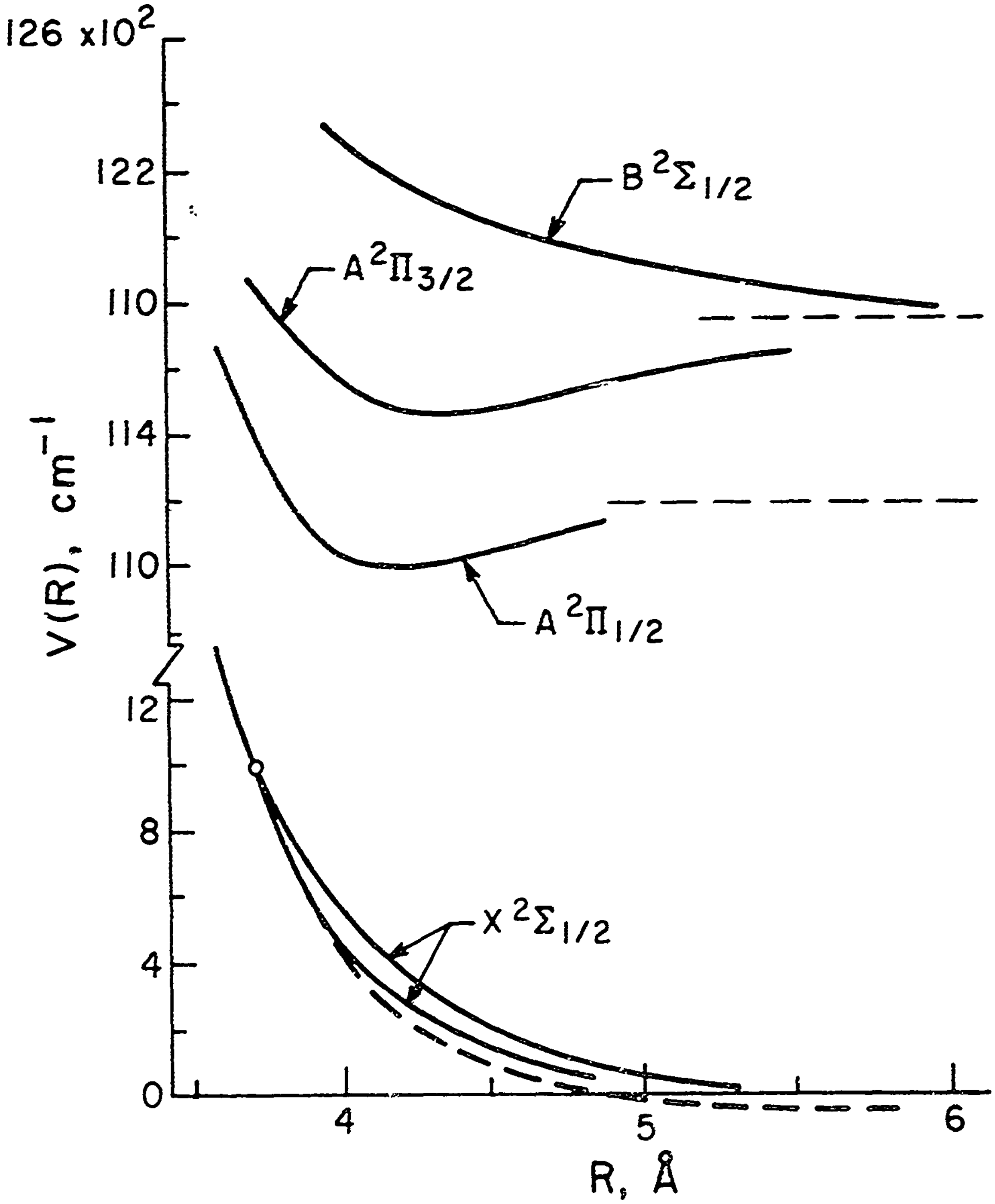

Fig. 4. Potential energy curves for CsAr molecule derived by Hedges, Drummond and Gallagher (Ref. 6) from spectral line profiles using quasistatic theory.

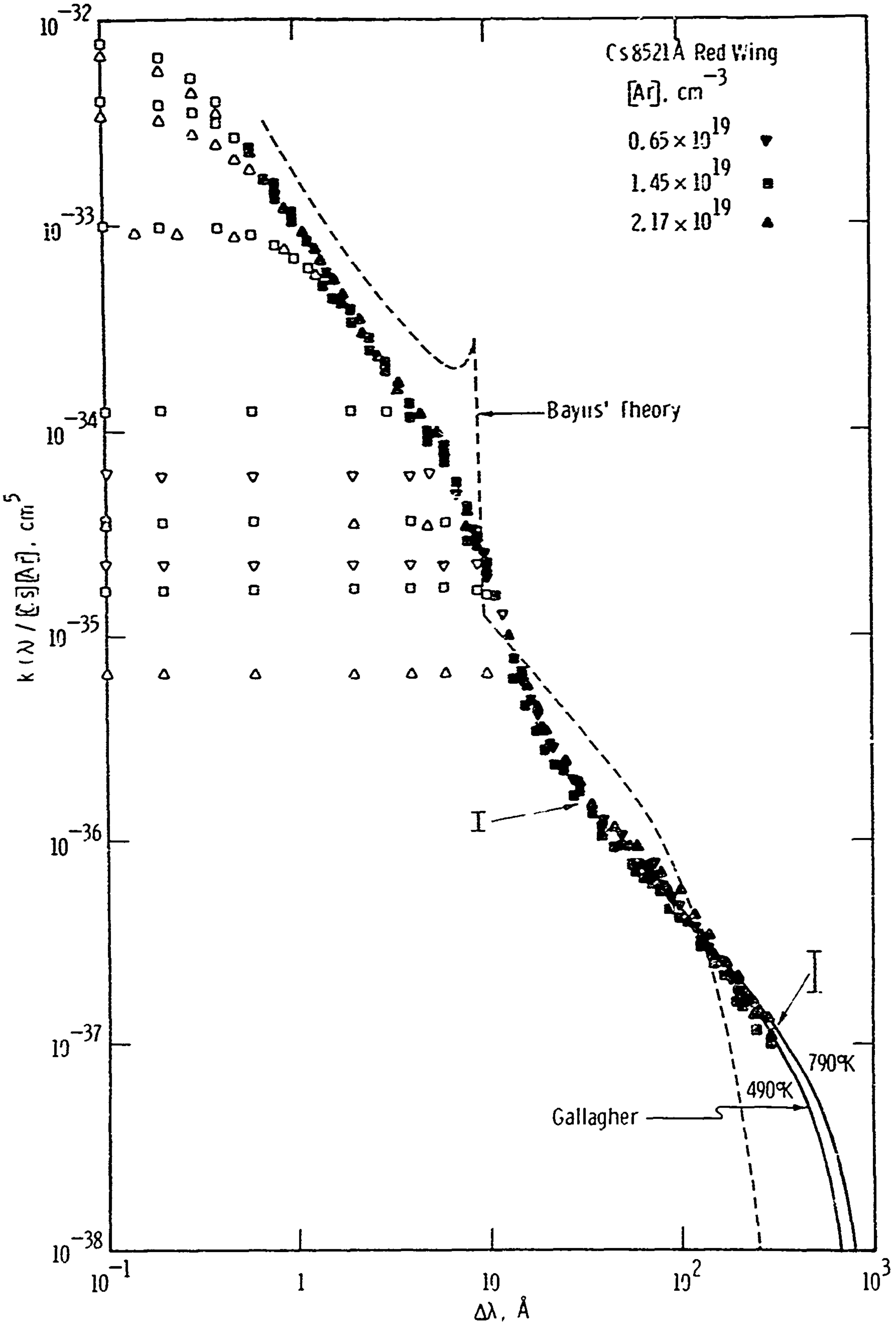

Fig. 5. Reduced absorption coefficients for the red wing of the Cs 8521 Å line broadened by argon. From Ref. 11.

III. PREDICTION OF STIMULATED EMISSION COEFFICIENT AND GAIN

In this section we consider the equations which allow us to predict the stimulated emission coefficients from the potential energy curves for the excited and ground state molecules. The gain per unit length of medium can be expressed in the form shown in Eq. (4) from Mitchell and Zemansky[12]:

$$g_\nu = \frac{\lambda^2}{8\pi} A_{u\ell} \left[\frac{\delta N_\nu^{u}}{\delta\nu} - \frac{g_u}{g_\ell} \frac{\delta N_\nu^{\ell}}{\delta\nu} \right] . \qquad (4)$$

Here δN_ν^u is the number of atoms in the upper state capable of radiating at a frequency and g_u and g_ℓ are the statistical weights of the upper and lower levels of the atom. Similarly, δN_ν^ℓ is the number of atoms in the lower state which are capable of absorbing the frequency ν. Using the quasistatic models discussed in connection with the fluorescence experiments, we can immediately write down expressions for $\delta N/\delta\nu$. Such an expression for the $\delta N/\delta\nu$ appropriate to the upper level of the molecule is

$$\frac{\delta N_\nu^{u,j}}{\delta\nu} = \frac{4\pi R^2(\nu)\cdot \delta R(\nu)}{\delta\nu} N_o \times P_j \times N_u \qquad (5)$$

$$= \frac{4\pi R^2(\nu)}{\left.\frac{\delta\nu}{\delta R}\right|_\nu} N_o \times \frac{g_{ju}}{g_{fu}} \exp\left(-\frac{\Delta V_u}{kT_v}\right) \times \frac{g_u}{g_\ell} N_\ell \exp\left(-\frac{\Delta V_o}{kT_e}\right) .$$

Here ΔV_o is the energy difference between the ground state and the excited state of the atom. Note that here we have expressed the Boltzmann factor giving relative populations of molecules in various vibrational states of the excited state in terms of a vibrational temperature T_v. This is consistent with our assumption of a complete equilibrium between the bound and free states when we take the vibrational temperature equal to the translational temperature of the gas. Also we have expressed the excited state population N_u as a function of the ground state population N_ℓ using an excitation temperature T_e. Substituting Eq. (5) and the corresponding equation for the lower state into Eq. (4) we obtain an expression for the gain:

$$\frac{g_u}{N_o N_\ell} = \alpha_u(\nu,T_u)\left[1 - \exp\left\{-\frac{(\Delta V_e-\Delta V_u)}{kT_v} + \frac{\Delta V_o}{kT_e}\right\}\right] . \qquad (6)$$

Here ΔV_ℓ is the increase in potential energy of the ground state from its value at infinite separation; α_u is a reduced stimulated emission coefficient and is a function of frequency and temperature. When multiplied by the product of the ground state density for the alkali and the perturber density, one obtains the stimulated emission portion of the gain per unit length. When multiplied by the exponential factors inside the square bracket one obtains the absorption contribution to the gain. The inversion condition is obtained by setting the exponential equal to unity and can be written as

$$\frac{\nu_o - \nu}{\nu_o} \geq \frac{T_v}{T_e} . \qquad (7)$$

Here $\nu_o = \Delta V_o/h$ is the frequency of the unperturbed radiation from the atom. This relation has been given previously by Carbone and Litvak[3] and simply says that in order to observe stimulated emission the ratio of the difference between the unperturbed frequency and the frequency of interest to the unperturbed frequency must be equal to or greater than the ratio of the vibrational-translational temperature to the excitation temperature of the atom. This relationship shows that one does not really need a repulsive ground state although the presence of a repulsive ground state certainly contributes to a large value for $\nu_o-\nu$ and makes it easy to maintain a Boltzmann population of lower state molecules at the translational temperature of the gas.

A. The LiXe molecule

We now ask whether some of the alkali rare gas molecules are good candidates for use in association lasers. Figure 6 shows the potential energy curve calculated for the lithium-xenon molecule by Baylis.[10] These are Baylis' original calculations and, on the basis of the work of Hedges, Drummond, and Gallagher,[6] would appear to be more nearly correct than his later calculations.

Equations (5) and (6) can be used to calculate the contributions of the absorption and stimulated emission terms to the gain. The results of such a calculation are shown in Fig. 7. These calculations have been made for a vibrational-translational temperature of 900°K and an excitation temperature for the atoms of 4000°K. The choice of vibrational-translational temperature is dictated by the probable requirements for a rather high vapor pressure of lithium in a laser system. The left hand abcissa shows values of the reduced gain and of the reduced stimulated emission and absorption coefficients for the lithium-xenon system. In both cases the coefficients are normalized to the ground state lithium density. We see that for the temperatures chosen, gain is predicted at wavelengths between about 8600 Å and 10500 Å. The peak value of the reduced gain coefficient occurs at 9500 Å and is about 3×10^{-39} cm^5. This means that if we wish to construct a laser with a gain of 1% per centimeter we require that the product of the ground state lithium density and the ground state xenon density be equal to 3×10^{36} cm^{-5}. If we assume a xenon density of 10^{20} atoms/cm^3 corresponding to about 10 atmospheres at 900°K, the ground state lithium density required is 3×10^{16} atoms per cubic centimeter corresponding to approximately 3 Torr at 900°K. For these conditions the

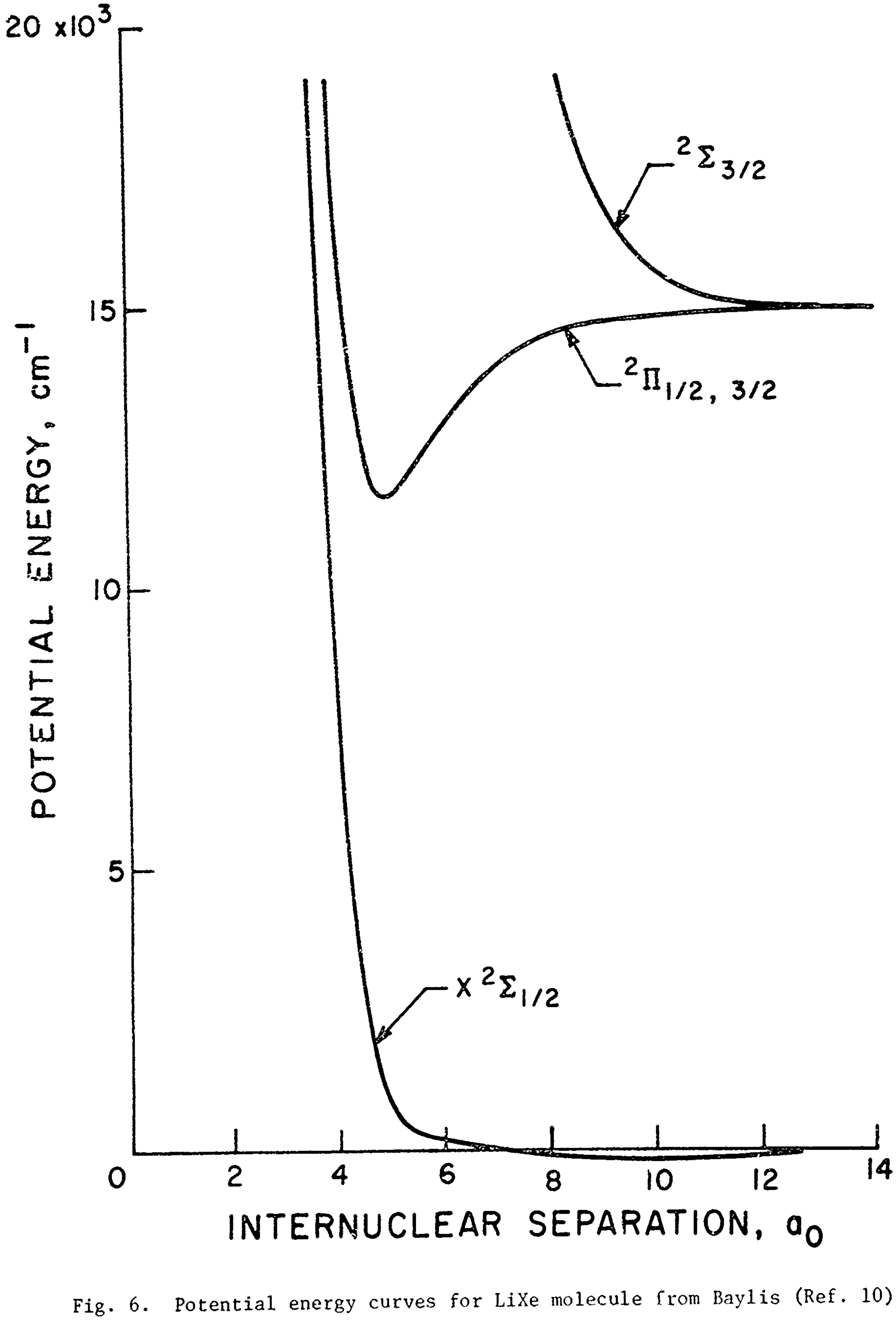

Fig. 6. Potential energy curves for LiXe molecule from Baylis (Ref. 10).

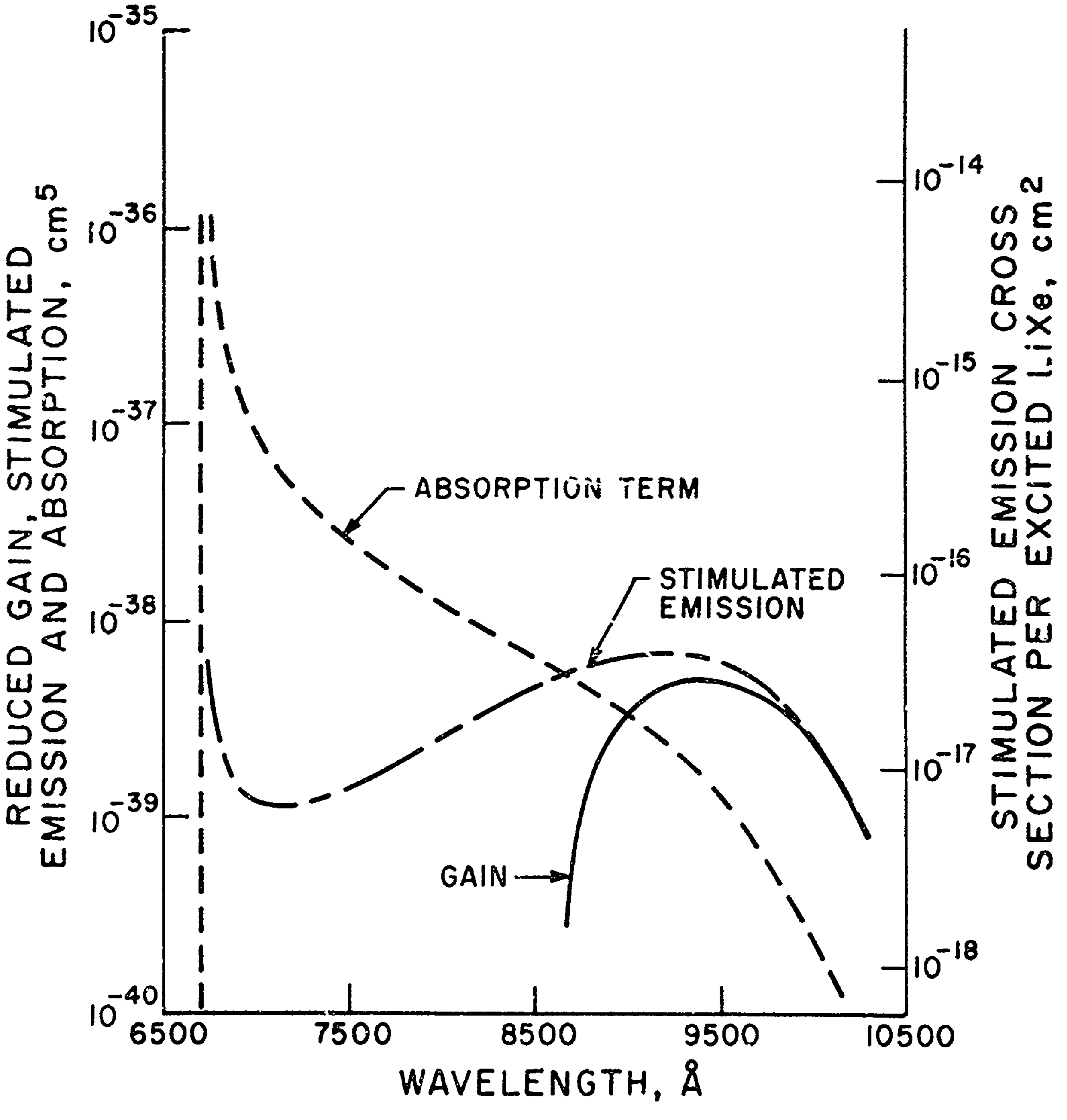

Fig. 7. Predicted reduced gain, stimulated emission and absorption for LiXe at T_v = 900°K and T_e = 4000°K. Right-hand scale is predicted stimulated emission cross section per excited molecule.

equilibrium densities of excited molecules and excited atoms are about equal so that imprisonment effects[13] are not very important. Therefore the effective lifetime of the excited states against spontaneous radiation is only a few times the natural lifetime and collisional destruction by Li_2, for example, should be unimportant.

Processes which compete directly with the stimulated emission are photoionization and photoabsorption by the excited molecules. One can estimate the importance of these processes by re-expressing the stimulated emission coefficient in terms of a cross section per excited molecule as indicated by the abscissa on the right side of the graph. For this purpose we have calculated the equilibrium constant for the $Li^* + Xe \rightleftarrows (LiXe)^*$ reaction using molecular constants obtained by fitting a Morse potential to the potential energy curve for the $(LiXe)^*$ molecule.[14] According to these calculations, the stimulated emission cross section per molecule at 9500 Å is approximately 3×10^{-17} cm^2. Since the threshold for photoionization of the $3\,^2\Pi$ states of LiXe is expected to be below 4000 Å, absorption of the stimulated emission is expected to be important only at wavelengths corresponding to bound-bound molecular transitions or to photoionization of highly excited states.[15]

B. The Xe_2 molecule

In the case of the xenon molecule, we do not have any detailed calculations of potential energy curves. There are, however, recent measurements of absorption as a function of the gas temperature by Kosinskaya and Polozova[16] (KP). In principle, these data can be used to calculate stimulated emission coefficients using the relations discussed in Eq. (6), i.e., these authors measure $\alpha_u(\nu,T)$ times the exponential terms in Eq. (6) for conditions where $T_v = T_e$ and $h\nu = \Delta V_o - \Delta V_\ell + \Delta V_u$. Unfortunately the available graph of these data is so small as to make the results almost meaningless. We have therefore taken potential energy curves constructed from data given by KP and used these to predict the stimulated emission coefficients. Figure 8 shows the reduced absorption coefficient calculated from the data of KP. Figure 9 shows potential energy curves constructed from various sources for the xenon molecule. The dashed curve is constructed from information given in a recent paper by Mulliken.[17] The solid curves are calculated from data given by KP.

Figure 10 shows the results of calculations carried out at 870°K in order to give a comparison between cross sections calculated from potential curves and from absorption data. The upper solid curve shows the stimulated emission coefficient $\alpha(\nu,T)$ as a function of wavelength as calculated from the solid curves of Fig. 9. The peak near 1750 Å is the result of parallel curves for the excited and ground states. As indicated previously, this singularity is indicative of a failure of the quasistatic model and we expect the spectral distribution to be much smoother than indicated in this graph. The lower solid curve is calculated from the data of KP and shows a much more rapid increase with wavelength than does the stimulated emission coefficient calculated from the potential curves. In fact, the $\alpha(\nu,T)$ curve calculated from the absorption data becomes impossibly large near 1750 Å. This unrealistic behavior may be the result of difficulties in reading absorption coefficients from the graph given by Kosinskaya and Polozova. The dashed curves are the results of measurements of fluorescent intensity at high pressures by Stewart, _et al._[18] and by Freeman, _et al._[19] These are relative curves and so can only be used to compare our theoretical calculations as to relative intensity as a function of wavelength. We see that both of these curves peak at shorter wavelengths than do our calculations. We have not attempted to readjust

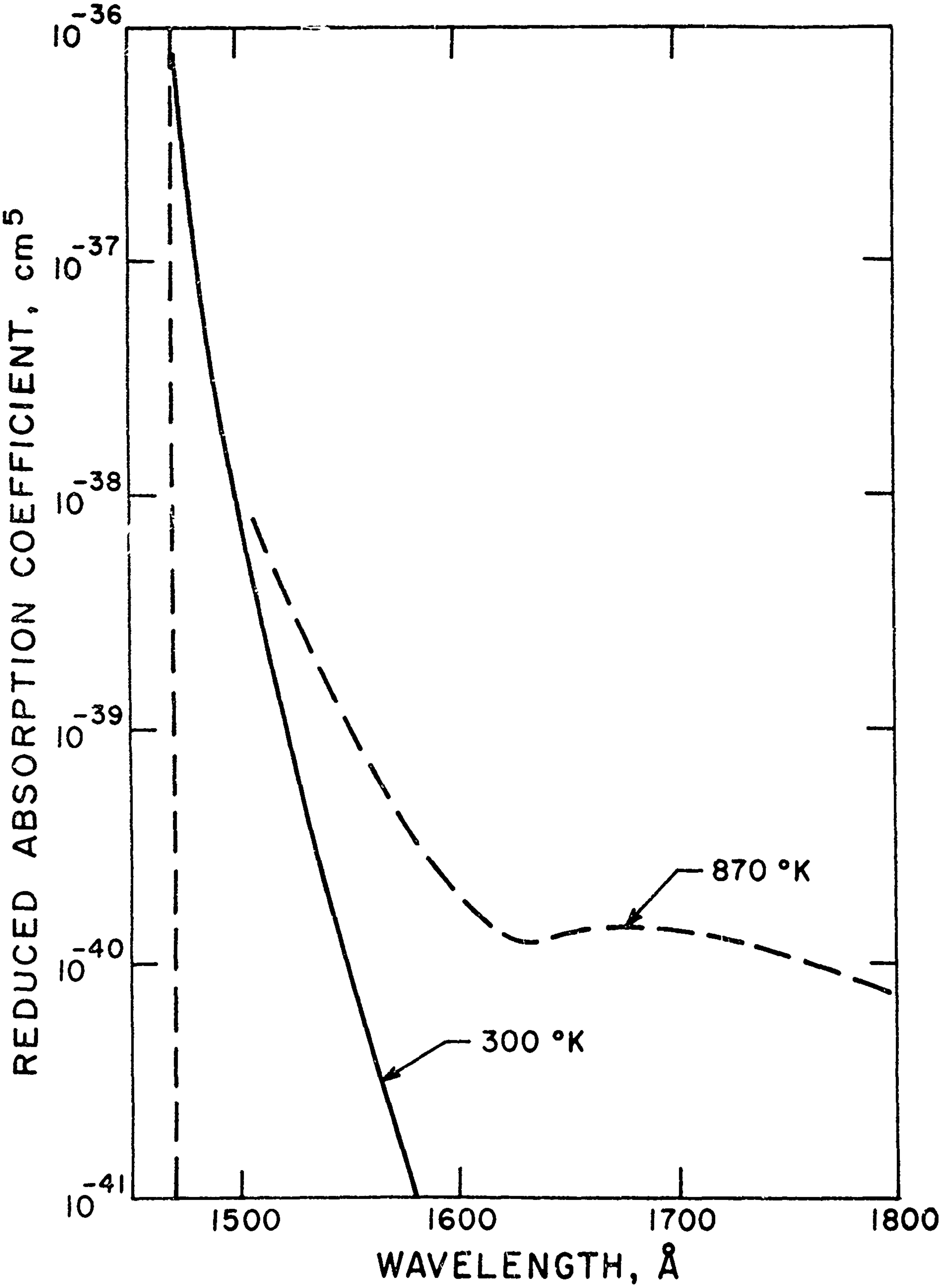

Fig. 8. Measured reduced absorption coefficients for xenon at various temperatures. From Ref. 16.

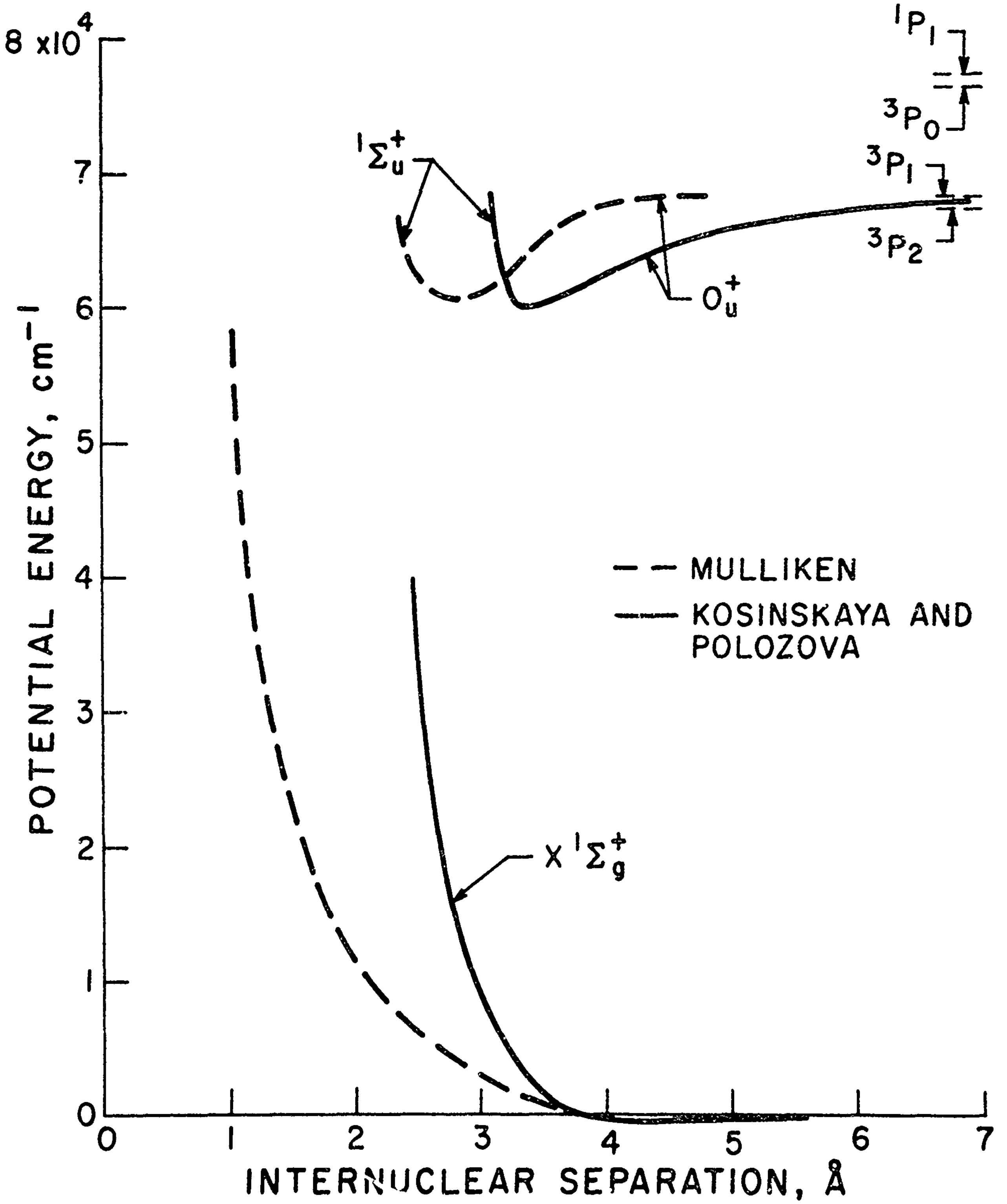

Fig. 9. Potential energy curves for lowest radiating state and ground state of Xe_2 molecule based on Mulliken (Ref. 17) and on Kosinskaya and Polozova (Ref. 16).

our potentials to obtain better agreement with these experimental data. since more than one excited state may be involved.

As in the case of LiXe, it is sometimes useful to express the results of the calculations in terms of the stimulated emission cross section per excited molecule. For the temperature and potential energy curves of the calculations of Fig. 10, the stimulated emission cross section per excited molecule is 10^{17} cm^{-3} times the values of the reduced coefficient given in Fig. 10, i.e., the stimulated emission cross section near the peak is about 10^{-17} cm^{2}. Note that as the gas temperature is lowered the width of the peak in the wave dependence of the stimulated emission coefficient will become narrower but the area under the curve will remain approximately constant.

Using the curves of Fig. 10 one estimates that an excited molecule density of 10^{14} to 10^{15} atoms/cm^{3} will be required in order to obtain a gain of 1%/cm. If the xenon pressure is high enough to maintain equilibrium among the vibrational states[6] of the excited molecule and is 10^{20} atom/cm^{3} at 870°K, then an excited atom density of 10^{11} to 10^{12} atoms/cm^{3} is required for the same gain. This corresponds to an excitation temperature for the excited state of atomic xenon of about 2400°K. Because of the rather deep potential well for the excited Xe molecules (1eV) and the resultant small excited atom densities, this expression of the requirements for gain in terms of the excited atom density may not be very useful.

C. The HeH molecule

Figure 11 shows the results of calculations of stimulated emission cross sections per excited molecule for the helium hydrogen system. In this case, the discrete nature of the vibrational states of the excited molecule is expected to be very important in that the vibrational

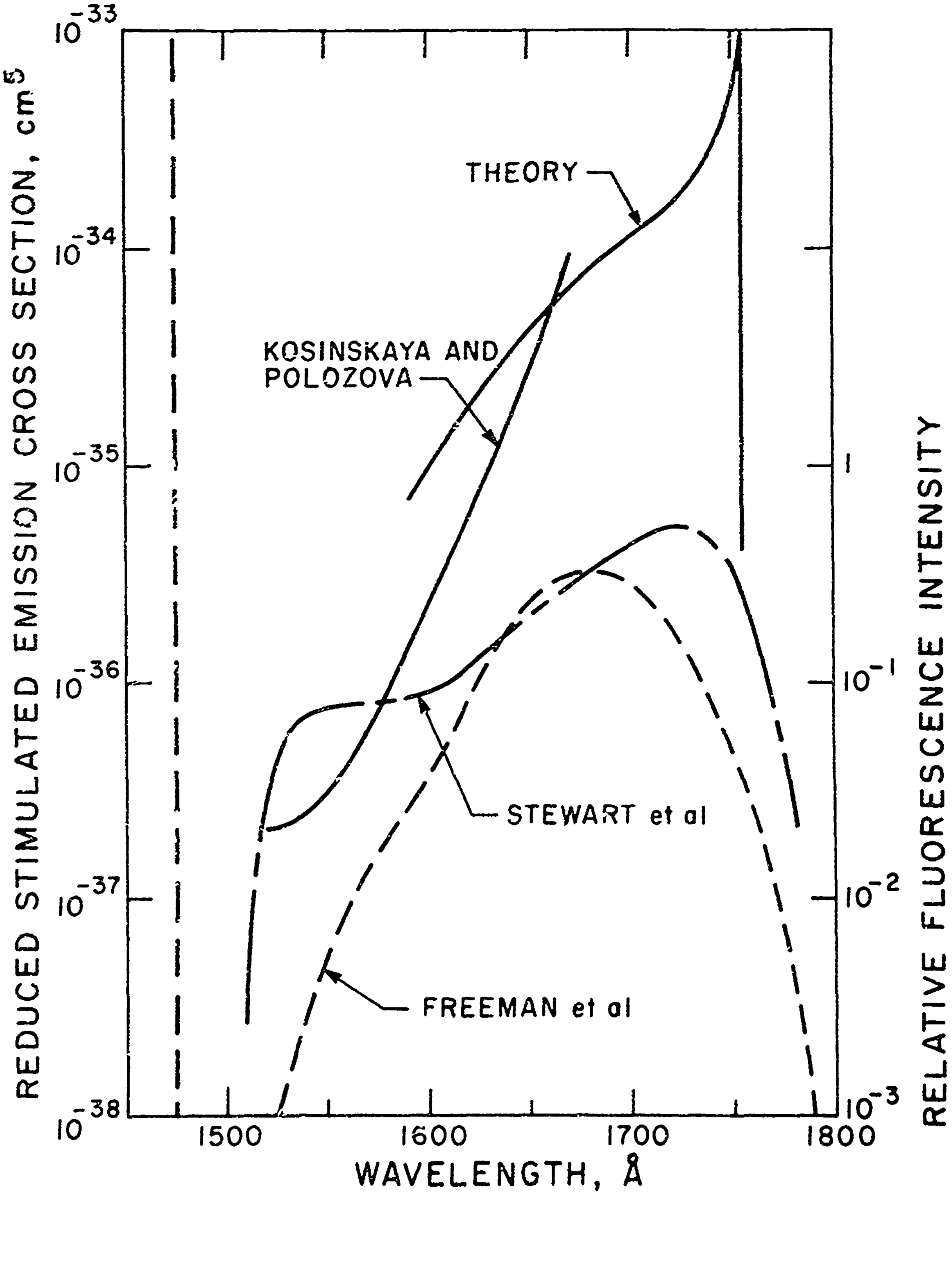

Fig. 10. Calculated reduced stimulated emission cross section (solid curves) and relative fluorescence (broken curves).

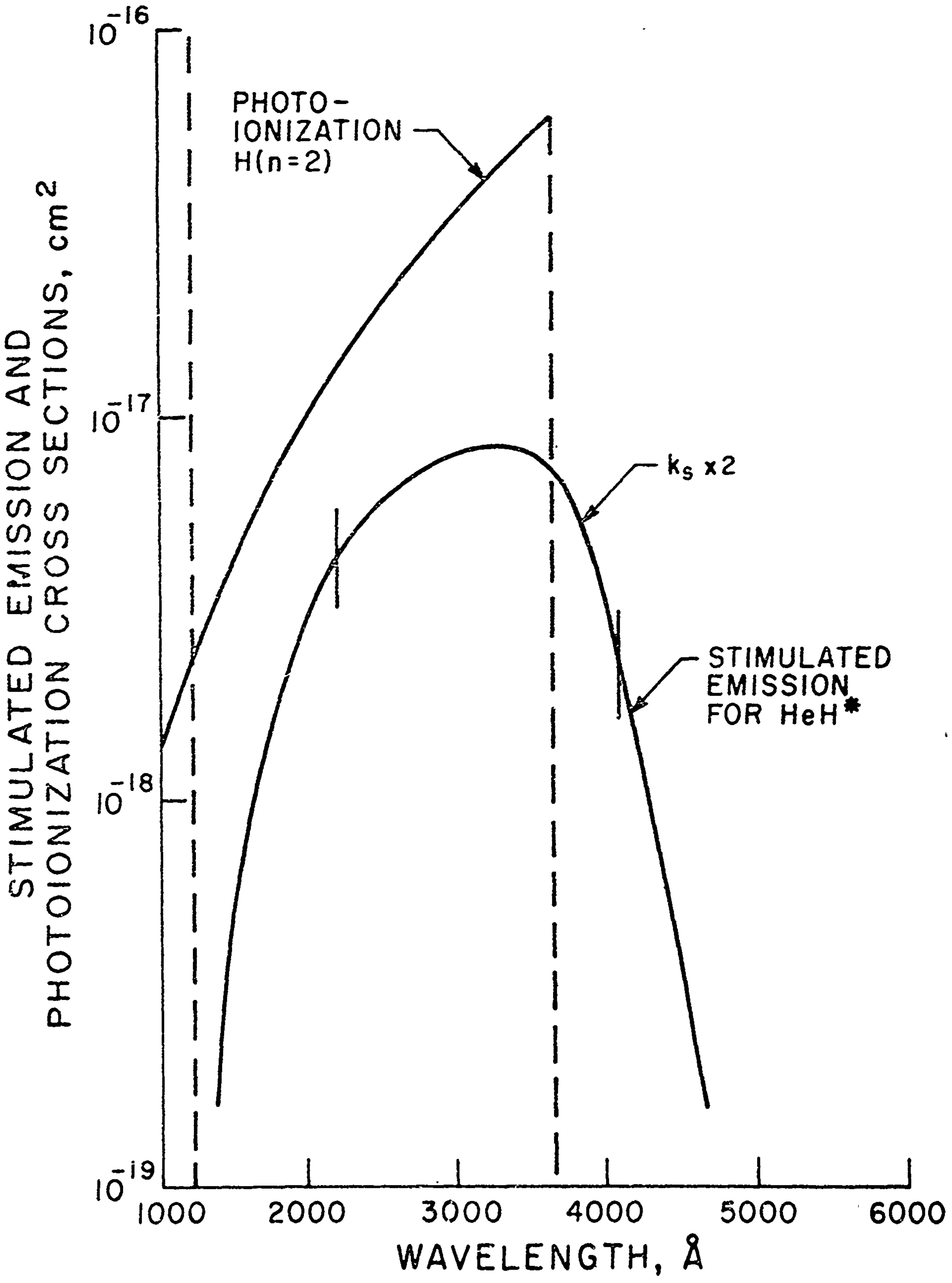

Fig. 11. Predicted stimulated emission cross section per excited LiH molecule and theoretical (Ref. 4) photoionization cross section for the n = 2 level of atomic hydrogen.

states will be relatively widely separated. This has the effect of preventing the accumulation of excited molecules in the bottom of a potential well, as predicted by the classical theory. In order to simulate the effect of the large radial extent of the lowest vibrational level, we have made our calculations for a vibrational temperature of 3000°K. We observed that the stimulated emission coefficient is roughly constant for wavelengths between 2000 and 4000 Å. The vertical bars indicate the wavelengths corresponding to the classical turning points of the lowest vibrational state and suggest that our use of a temperature of 3000°K simulates reasonably well the spread in internuclear separations covered by the ground vibrational state. In order to estimate the effects of photoionization of the excited molecules, we have shown the photoionization of cross sections appropriate to the first excited state of atomic hydrogen.[4] We observed that if the cross section for photoionization of HeH were as large as that for atomic hydrogen, the absorption coefficient would exceed the stimulated emission in molecular hydrogens. However, Michels[9] has pointed out that the photoionization cross section for a Rydberg state, such as we are discussing here, is expected to be much lower than that for the corresponding state of atomic hydrogen.

IV. DISCUSSION

The preceding sections have shown how a very simple theory of spectral line broadening can be used to predict laser gain in specific systems which make use of stimulated transitions from attractive upper molecular states to repulsive lower states. In this section we will make a few generalizations and recommendations for further work.

a) From the preceding calculations for LiXe, Xe_2 and HeH one notes that the stimulated emission cross sections for these species are roughly 10^{-17} cm^2 per excited molecule. Such values are expected[14] from the relation between the integrated absorption coefficient and the oscillator strength[12] for the highly allowed transitions, such as considered in our calculations. Since much larger excited molecule densities would be required for stimulated emission involving partially forbidden molecular transitions, the allowed transitions considered above seem to offer the best possibilities for laser operation.

b) The techniques used here for transitions between bound and continuum levels may be of some use for bound-bound molecular transitions. Of course, it will then be necessary to take into account the breaking up of the continuum into the large number of collision broadened rotational and vibrational transitions.

c) A considerable improvement in the accuracy of the predictions of stimulated emission coefficients and cross sections near the singular peaks, e.g., near 1750 Å, in Fig. 10, is expected when the recently developed[20] solutions for these regions become fully available. In one form, these are approximate solutions for the spectral dependence of the intensity in terms of Airy functions with fitting parameters determined from the potential energy curves.

d) The calculation of laser gain is even less certain than the calculation of the reduced stimulated emission and absorption coefficients or cross sections because of the lack of information regarding production and destruction processes for the excited atoms and molecules. In addition to the quantitative fluorescence and absorption measurement discussed above, one can learn much of use in such calculations by time-dependent fluorescent and absorption studies. It is indeed amazing that in spite of hundreds of papers[21] on excitation transfer to various atoms and molecules in mercury vapor there are no clear-cut demonstrations of the origin of 3350 and 4850 Å bands of pure mercury. The situation in the rare gases is slightly better as the result of reasonably complete studies of the destruction mechanisms for the atomic metastables.[22] The need for further information regarding rare gas molecules is evidenced by uncertainty in the xenon molecular potential energy curves in Fig. 9. Also, there is an almost complete lack of information regarding processes of importance at high energy densities, e.g., metastable-metastable collisions, photoionization of highly excited atomic and molecular levels, and electron impact excitation and neutral particle relaxation of the vibrational levels of the excited molecules. The conditions for equilibrium among the vibrational levels of the excited state are currently being investigated by Gallagher[23] for several alkali-rare gas systems. Some data for $He_2(a^3\Sigma_u^+)$ have been obtained by Callear and Hedges.[24] The fluorescence data of Rhodes[25] may also be capable of providing vibrational relaxation data for the rare gas molecules.

V. ACKNOWLEDGEMENTS

The author is particularly indebted to A. C. Gallagher of JILA for helpful discussions of this subject. He also wishes to thank numerous scientists for contributing helpful comments and references during the course of visits to other laboratories, e.g., NRL, AFWL and LLL.

REFERENCES

1. N. G. Basov, V. A. Danilychev, and Yu. M. Popov, Krantoraya Électronika 1, 29 (1971) [translation: Soviet J. Quantum Electronics 1, 181 (1971)];

   N. G. Basov, Paper D-6, VIIth Int'l. Quantum Electronics Conf., Montreal, May 1972.
2. H. A. Koehler, L. J. Ferderber, D. L. Redhead and P. J. Ebert, Appl. Phys. Letters (submitted, 1972).
3. R. J. Carbone and M. M. Litvak, J. Appl. Phys. 39, 2413 (1968).
4. A. J. Palmer, J. Appl. Phys. 41, 438 (1970).
5. H. Kuhn, Phil. Mag. 18, 987 (1934); H. Margenau and W. W. Watson, Rev. Mod. Phys. 8, 22 (1936); D. R. Bates, Monthly Notices Roy. Astron. Soc. 112, 40 (1952).
6. R. E. M. Hedges, D. L. Drummond and A. Gallagher, Phys. Rev. A (in press, 1972).
7. W. Behmenberg, Z. Naturforsch. 27a, 31 (1972).
8. C. A. Slocomb, W. H. Miller and H. F. Schaefer III, J. Chem. Phys. 55, 926 (1971).
9. H. H. Michels, private communication.
10. W. E. Baylis, J. Chem. Phys. 51, 2665 (1969).
11. C. L. Chen and A. V. Phelps, Bull. Am. Phys. Soc. 15, 1528 (1970) and Phys. Rev. A (submitted, 1972).
12. A. C. G. Mitchell and M. W. Zermansky, *Resonance Radiation and Excited Atoms* (Cambridge Univ. Press, Cambridge, 1934), Chap. 3.
13. T. Holstein, Phys. Rev. 72, 1212 (1948) and 83, 1159 (1951).
14. G. Herzberg, *Spectra of Diatonic Molecules* (D. Van Nostrand Co., Inc., New York, 1950) and *Infrared and Raman Spectra* (D. Van Nostrand Co., Inc., New York, 1945).

15. D. E. Rothe, J. Quant. Spectrosc. Radiative Transfer 11, 355 (1971).

16. I. V. Kosinskaya and L. P. Polozova, Opt. Spectrosc. 30, 458 (1971).

17. R. S. Mulliken, J. Chem. Phys. 52, 5170 (1970).

18. T. E. Stewart, et al., J. Opt. Soc. Am. 60, 1290 (1970).

19. C. G. Freeman, et al., Chem. Phys. Letters 10, 530 (1971).

20. K. Sando, private communication.

21. R. J. Cventanović, in Progress in Reaction Kinetics, G. Porter, editor (The Macmillan Company, New York, 1964).

22. See for example, A. V. Phelps, Phys. Rev. 114, 1011 (1959); E. Ellis and N. D. Twiddy, J. Phys. B: Atom. Molec. Phys. 2, 1366 (1969); R. Turner, Phys. Rev. 140, A426 (1965); W. Wieme and P. Mortimer, Proc. 10th Int'l. Conf. Ionization Phonomena in Gases, Oxford, 1971.

23. A. C. Gallagher, private communication.

24. A. B. Callear and R. E. M. Hedges, Trans. Faraday Soc. 66, 2921 (1970).

25. C. K. Rhodes, private communication.