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0521019672 - Collision-Induced Absorption in Gases
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Introduction

Spectroscopy is concerned with the interaction of light with matter. This monograph deals with *collision-induced* absorption of radiation in gases, especially in the infrared region of the spectrum. Contrary to the more familiar *molecular* spectroscopy which has been treated in a number of well-known volumes, this monograph focuses on the *supermolecular* spectra observable in dense gases; it is the first monograph on the subject.

For the present purpose, it is useful to distinguish molecular from supermolecular spectra. In ordinary spectroscopy, the dipole moments responsible for absorption and emission are those of individual atoms and molecules. Ordinary (or allowed) spectra are caused by *intra*-atomic and *intra* molecular dynamics. Collisions may shift and broaden the observable lines, but in ordinary spectroscopy collisional interactions are generally not thought of as a *source* of spectral intensity. In other words, the integrated intensities of ordinary spectral lines are basically given by the square of the dipole transition matrix elements of individual molecules, regardless of intermolecular interactions that might or might not take place. Supermolecular spectra, on the other hand, arise from interaction-induced dipole moments, that is dipole moments which do not exist in the individual (i.e., non-interacting) molecules. Interaction-induced dipole moments may arise, for example, by polarization of the collisional partner in the electric multipole field surrounding a molecule, or by intermolecular exchange and dispersion forces, which cause a temporary rearrangement of electronic charge for the duration of the interaction. The existence of interaction-induced dipole moments and the associated collision-induced absorption (emission), i.e., radiation processes involving more than just one molecule, is a well established fact.

The concept of supermolecules is a most useful one for any detailed treatment of interaction-induced processes. If gases are considered with densities which, on the one hand, are well below liquid density so that many-body effects are minimized but, on the other hand, high enough so that supermolecular effects are observable, a virial expansion of the dielectric and spectroscopic bulk properties in powers of gas density n may be possible. In that case, one need not consider the complex many-body system consisting of all molecules of the fluid. Instead, one has a sequence of relatively simple two-, three-, ... body Hamiltonians which represent the supermolecules of interest. A few leading Hamiltonians may model the spectroscopic properties of the whole system accurately if densities are not too high.

For the purpose of this work, we will call a complex of two or more interacting atoms/molecules a supermolecule. Supermolecules may exist for a short time only, e.g., the duration of a fly-by encounter ($\approx 10^{-13}$ s). Alternatively, supermolecules may be bound by the weak van der Waals forces and thus exist for times of the order of the mean free time between collisions ($\approx 10^{-10}$ s), or longer. In any case, it is clear that, in general, supermolecules possess a spectrum of their own, in excess of the sum of the spectra of the individual (non-interacting) molecules that make up the supermolecule. These spectra are the collision-induced spectra, the subject matter of this monograph.

Conventional molecular spectra arise typically from transitions between the rotovibrational (i.e., bound) states. Collision-induced spectra, on the other hand, involve transitions principally between free (i.e., translational or unbound) states. The translational state of a pair of atoms is given by the energy, E, and angular momentum, L^2, L_z, of relative motion. These quantities are analogous to the vibrational energy, E_v, and rotational angular momentum, J^2, J_z, of bound diatomics; translational energies are, however, continuous while vibrational energies are discrete. The translational spectra of supermolecules involve diffuse lines resembling continuous spectra which are centered at zero frequency and, if molecules are involved, at a number of other frequencies related to the rotovibrational states of the molecules of the complex.

It is a remarkable fact that the translational transitions of virtually all supermolecules are infrared active – even if the individual molecules are not. The only exceptions are supermolecules that possess a symmetry which is inconsistent with the existence of a dipole moment. Pairs of like atoms, e.g., He–He, have inversion symmetry, implying a zero dipole moment and, hence, infrared inactivity. But dissimilar atomic pairs, e.g., He–Ar, or randomly oriented molecular pairs, e.g., H_2–H_2, generally lack such symmetry. As a consequence, more or less significant collision-induced dipoles exist for the duration of the interaction which generate the well known collision-induced spectra.

It was mentioned above that the individual molecules of a complex will usually be unbound particles in collisional interaction, but we note that spectral components involving induced radiative transitions of bound complexes, e.g., HeAr or $(H_2)_2$, the so-called van der Waals molecules, are really inseparable from those of collisional complexes and will, therefore, be of considerable interest here as well.

Molecular and electronic spectra. Two kinds of molecular spectra are generally distinguished: rotovibrational and electronic spectra. Examples of the *rotovibrational* spectra are the purely rotational bands, and the fundamental and overtone bands, of polar molecules like CO; these appear in the far and near infrared, respectively. On the other hand, examples of an *electronic* spectrum are the Schumann–Runge bands of molecular oxygen which correspond to transitions from the ground state, ${}^3\Sigma_g^-$, to some excited state, ${}^3\Sigma_u^-$, the highest electronic state shown in Fig. 7.1, p. 357. These bands converge to a limit at 56 850 cm^{-1} (that is 7.047 eV) and become continuous at higher frequencies. Electronic spectra generally appear at the higher frequencies of the electromagnetic spectrum, typically in the visible and ultraviolet.

Supermolecular spectra may also be of the electronic or rotovibrational type. This book deals with the rotovibrational types, which should perhaps be called rovibro-translational spectra to express the significant involvement of translational transitions of supermolecular systems. Even if the molecules by themselves are infrared inactive, the translational motion will generally be infrared active. Supermolecular electronic spectra exist but are not as universal as the rotovibrational induced spectra. Collision-induced electronic spectra will be briefly considered in Chapter 7.

Binary and ternary spectra. We will be concerned mainly with absorption of electromagnetic radiation by binary complexes of inert atoms and/or simple molecules. For such systems, high-quality measurements of collision-induced spectra exist, which will be reviewed in Chapter 3. Furthermore, a rigorous, theoretical description of binary systems and spectra is possible which lends itself readily to numerical calculations, Chapters 5 and 6. Measurements of binary spectra may be directly compared with the fundamental theory. Interesting experimental and theoretical studies of various aspects of *ternary* spectra are also possible. These are aimed, for example, at a distinction of the fairly well understood pairwise-additive dipole components and the less well understood ‘irreducible’ three-body induced components. Induced spectra of bigger complexes, and of reactive systems, are also of interest and will be considered to some limited extent below.

A collisional complex interacts with radiation for short times only, roughly 10^{-13} s, the duration of a molecular fly-by encounter. We may say that collisional complexes ‘exist’ for short times only. Nevertheless, supermolecules are a physical reality. Spectra of other species having

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short lifetimes are, of course, well known. For example, we have radiative transitions involving pre-dissociating molecules (where the final state exists for only $\approx 10^{-12}$ s), radicals (which are chemically unstable and likely to react in the first suitable collision) and van der Waals molecules (which are so weakly bound that the first collision often breaks them up). Collisionally interacting systems and their spectra are just as real as the examples given.

Supermolecular spectra could perhaps be studied with state-selection using adequate molecular beam techniques. That would not be easy, however, because of the smallness of the dipole moments induced by intermolecular interactions. For the purpose of this book, we will mostly deal with bulk spectra, or interaction-induced absorption of pure and mixed gases. A great variety of excellent measurements of such spectra exists for a broad range of temperatures, while state-selected supermolecular absorption beam data are virtually non-existent at this time. Furthermore, important applications in astrophysics, etc., are concerned precisely with the optical bulk properties of real gases and mixtures.

Spectroscopic techniques have been applied most successfully to the study of individual atoms and molecules in the traditional spectroscopies. The same techniques can also be applied to investigate intermolecular interactions. Obviously, if the individual molecules of the gas are infrared inactive, induced spectra may be studied most readily, without interference from allowed spectra. While conventional spectroscopy generally emphasizes the measurement of frequency and energy levels, collision-induced spectroscopy aims mainly for the measurement of intensity and line shape to provide information on intermolecular interactions (multipole moments, range of exchange forces), intermolecular dynamics (time correlation functions), and optical bulk properties.

Real gases. This book deals with the spectra of *real* (as opposed to *ideal*) gases, that is gases composed of real atoms or molecules which interact not only with electromagnetic radiation, but also with the other atoms and molecules of the gas.

One may argue that the traditional spectroscopy is the spectroscopy of *ideal* gases: Intensities of ordinary spectra are generally not thought of as being significantly enhanced or altered by intermolecular interactions. The concept of an ideal (or 'perfect') gas composed of non-interacting particles ('mass points') is familiar from the kinetic theory of gases. It constitutes, of course, a highly simplified, but most useful model that permits an understanding of certain basic properties of gases. For example, the relationship between pressure, p, density, n, and temperature, T,

$$p = nkT \ ,$$

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the *ideal gas law*, is well verified experimentally in the low-pressure limit; k designates Boltzmann's constant.

Real gases, on the other hand, consist of atoms or molecules that interact through intermolecular forces. Atoms/molecules attract at distant range and repel at near range; they may be thought of as having a finite size. The theory of real gases accounts for these facts by means of a *virial* expansion,

$$p = A\,n + B\,n^2 + C\,n^3 + \dots \tag{1.1}$$

In other words, the equation of state may be written as a series in powers of density, with first, second, third, ..., virial coefficients given by

$$\begin{aligned} A &= kT\,, \\ B &= -2\pi kT \int_0^\infty \left[\exp\left(-\frac{V(R)}{kT}\right) - 1\right] R^2\,\mathrm{d}R\,, \\ C &= -\frac{kT}{3} \int\!\!\int f(R_{12})\; f(R_{13})\; f(R_{23})\; \mathrm{d}^3R_{12}\,\mathrm{d}^3R_{13}\,, \\ \dots & \quad \dots \end{aligned}$$

etc., with $f(R_{ij}) = \exp(-V(R_{ij})/kT) - 1$ and $\boldsymbol{R}_{23} = \boldsymbol{R}_{13} - \boldsymbol{R}_{12}$. These coefficients account for the effects of monomers and interacting pairs, triplets, ... of atoms or molecules; $V(R)$ designates the pair interaction potential as a function of internuclear separation, R.

In the broad vicinity of the low-pressure (or ideal gas) limit, induced spectra may also be represented in the form of of a virial expansion,

$$I = \widetilde{A}\,n + \widetilde{B}\,n^2 + \widetilde{C}\,n^3 + \dots \tag{1.2}$$

with coefficients representing the dipole-allowed monomer contributions ($\widetilde{A}$), and the induced binary ($\widetilde{B}$), ternary ($\widetilde{C}$), ..., spectral components. Intensities of spectra of ordinary atoms or molecules vary linearly with density, $I_{\text{allowed}} = \widetilde{A}n$: spectral intensities are proportional to the number of sources in the sample volume. Intensities of collision-induced spectra, on the other hand, typically vary with the second or higher powers of density, $I_{\text{induced}} = \widetilde{B}n^2 + \widetilde{C}n^3 + \dots$, i.e., these are proportional to the number of pairs, triplets, etc., in the sample volume.

Like the various terms of the virial expansion of the equation of state, the second and higher spectral virial terms in Eq. 1.2 are insignificant at low densities. They become significant, however, at sufficiently high density. At densities approaching liquid density, many-body interactions may be expected to dominate the optical properties. At such densities, each atom or molecule of the liquid is surrounded by a fairly large number of close neighbors, e.g., for liquid argon roughly twelve in the first shell and many more in the more distant 'shells'. Virial expansions are meaningless under such conditions. Other theories appropriate for liquid densities must then be used which, however, will not be considered in this work. We are concerned here mainly with small supermolecular complexes and densities where virial expansions are valid.

We will occasionally use the term ‘dense gas’ which is meant to describe a gas of a density high enough for induced spectra to appear. In more practical terms, this means roughly atmospheric densities or higher, but we hasten to add that even at much lower densities certain induced features are often discernible as will be seen below (Chapter 3). One atmosphere is certainly not a threshold below which all induced effects miraculously disappear.

1.1 Historical sketch

Spectroscopists are often concerned with the absorption of light in gases. Let I and I_0 be the transmitted and incident intensity of a light beam. The absorption coefficient $\alpha = \alpha(\nu\,; T, n)$ is defined by Lambert’s law,

$$I = I_0 \, \exp\left(-\alpha \, \Delta x\right) \, , \tag{1.3}$$

where Δx designates the optical path length and T the temperature. In many cases of practical importance, the absorption coefficient is proportional to the number density of the gas, $\alpha \propto n$ (Beer’s law). If the absorption coefficient is known as a function of frequency ν, it is usually referred to as the absorption spectrum.

Early work. In 1885, Janssen found that in oxygen at pressures of tens or hundreds of atmospheres new absorption bands occur which are unknown from absorption studies at atmospheric pressures; see pp. 357ff. for details. The associated absorption coefficients increase as the *square* of density, in violation of Beer’s law. The observed quadratic dependence suggests an absorption by *pairs* of molecules; Beer’s law, by contrast, attempts to describe absorption by individual molecules.

Interaction-induced absorption (as the new features were called early on [353]) has stimulated considerable interest. For a long time, explanations were attempted in terms of weakly bound $(O_2)_2$ ‘polarization’ molecules (that is, van der Waals molecules), but some of the early investigators argued that unbound *collisional pairs* might be responsible for the observed absorption. More recently, a study of the temperature dependence of the induced intensities has provided evidence for the significance of collisional complexes. The idea of absorption by collisionally interacting, unbound molecular pairs was, however, not widely accepted for decades.

A search and a find. Rotovibrational collision-induced absorption was discovered incidentally in a search for the elusive spectra of van der Waals molecules (‘dimers’). In his famous dissertation of 1873, J. D. van der

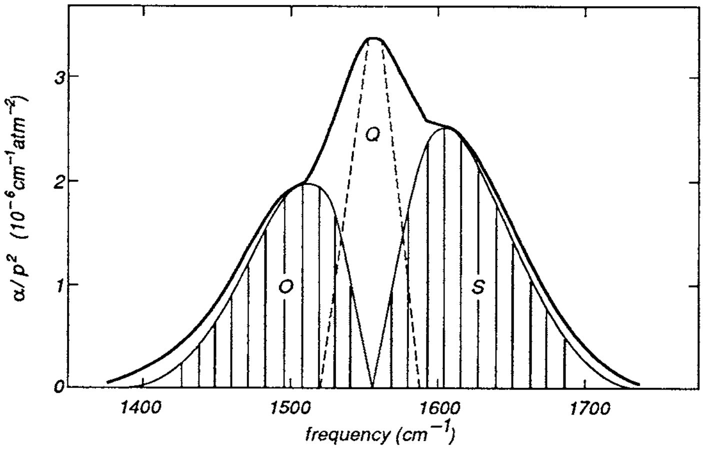

Fig. 1.1. Induced rotovibrational absorption of O_2 pairs. The heavy curve represents the measurement; the light curve is a theoretical envelope ('stick spectrum') of the Raman *O* and *S* branches. The envelope of the *Q* branch is shown as a broken line; after [128].

Waals postulated that intermolecular forces include an attractive component. Ever since then, the existence of weakly bound inert atoms or molecules has been conjectured. The brief remarks made above in connection with induced electronic transitions in oxygen involving hypothetical polarization molecules may serve as an illustration of a situation that has existed for generations. However, until fairly recently, direct evidence for the existence of van der Waals molecules was scant, and a knowledge of energy levels, spectra, etc., of dimers was slow in coming. In 1949, in an attempt to record the infrared vibrational absorption band of $(O_2)_2$ dimers, Welsh and associates [128] discovered instead marked absorption in compressed gases and in liquid oxygen, with a maximum at a frequency roughly equal to the vibrational frequency of the O_2 molecule, 1556 cm^{-1}, see the heavy curve, Fig. 1.1. Similarly, in compressed nitrogen, an absorption band was found with maximum absorption at the N_2 vibrational frequency, 2331 cm^{-1}. (Vibrational bands involving excitation from the ground state to the lowest excited vibrational level are referred to as fundamental bands.) Pressures up to 60 atmospheres were used; the absorption cell was 85 cm long. Subsequent work showed that such induced spectra, and also purely rotational and overtone spectra, exist for virtually all molecular gases. However, these were not the spectra of bound dimers the study had set out to find. The spectral features are diffuse and quite unlike the expected rotovibrational dimer bands.

Homonuclear molecules have a center of inversion symmetry. Molecular charge distributions of such symmetry are inconsistent with a permanent dipole moment. As a consequence, such molecules are infrared inactive unless they are perturbed by some external influence. Welsh and associates showed that the absorption varies precisely as the *square* of the density, a fact that suggests induced absorption by *pairs* of molecules which have symmetries that will in general be different from those of the molecules involved.

In the mixture of oxygen and nitrogen, all induced absorption bands, both of O_2 and N_2, were enhanced by the foreign gas addition, suggesting that at least in some cases an N_2 molecule is similarly capable in inducing the O_2 fundamental band when interacting with O_2, as an O_2 molecule is in inducing the N_2 fundamental band. As a rule, for most bands observed, almost *any* interacting partner is capable to induce these bands. Welsh and associates state emphatically, and subsequent studies have fully confirmed, that the observed absorption must have its origin in dipole transitions induced by intermolecular forces during collisions of *unbound* monomers; bound complexes like O_4 are *not* required for an explanation of the observed absorption bands (but must not be ruled out completely as we will see).

Hence, the process was named collision-induced absorption. Whereas the term 'interaction-induced absorption' used by some early on seems to cautiously leave the question open whether free or bound complexes generate the absorption, Welsh and associates bravely state their conclusion as collisional interactions. Since then, other names have also been used, such as pressure-induced and supermolecular absorption.

Figure 1.2 illustrates the difference between the transitions involved in van der Waals dimer bands which Welsh and associates hoped to find, and the collision-induced absorption spectra that were discovered instead. Intermolecular interaction is known to be repulsive at near range and attractive at more distant range. As a consequence, a potential well exists which for most molecular pairs is substantial enough to support bound states. Such a bound state is indicated in Fig. 1.2 (solid curve *b*). When infrared radiation of a suitable frequency is present, the dimer may undergo various transitions from the initial state (solid curve) to a final state which may have a rather similar interaction potential (dashed curve *b*′) and dimer level spacings. Such transitions (marked *bound–bound*) often involve a change of the rotovibrational state(s) E_{vj} of one or both molecule(s),

$$\Delta E = E_{v_1' j_1'} - E_{v_1 j_1} + E_{v_2' j_2'} - E_{v_2 j_2} \, , \tag{1.4}$$

as well as of the dimer. The dimer transition frequencies are relatively sharp unless gas pressures are high enough to broaden the dimer lines. Dimer transition frequencies are given by $h\nu = \Delta E + E'_{\text{bound}} - E_{\text{bound}}$. Such processes are known to give rise to absorption spectra of van der

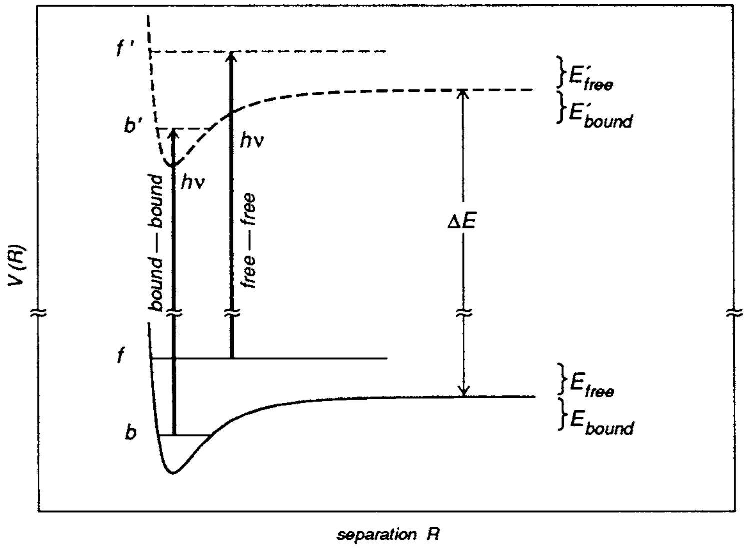

Fig. 1.2. Intermolecular potential curves and radiative transitions of the complex of molecules 1 and 2. The energy spacing $\Delta E = E_f - E_i$ is the difference of the rotovibrational energies of initial and final states of the complex, $E_i = E_{v_1 j_1} + E_{v_2 j_2}$ and $E_f = E'_{v_1 j_1} + E'_{v_2 j_2}$, respectively. The E_{bound} and E_{free} designate bound and free state energies of the complex; a prime indicates final states. Also shown are representative radiative transitions $h\nu$ from bound state to bound state, and from free state to free state, involving rotovibrational transitions in one or both molecules.

Waals molecules in the various rotovibrational bands of the individual molecules, and also at their sums and differences. The actual recording of such dimer bands is a fairly recent accomplishment [49, 268].

Welsh suggested correctly that similar transitions take place even if the molecular pair is not bound. The energy of relative motion of the pair is a continuum. Its width is of the order of the thermal energy, $E_{\text{free}} \approx 3kT/2$. Radiative transitions between free states occur (marked *free–free* in the figure) which are quite diffuse, reflecting the short 'lifetime' of the supermolecule. In dense gases, such diffuse collision-induced transitions are often found at the various rotovibrational transition frequencies, or at sums or differences of these, even if these are dipole forbidden in the individual molecules. The dipole that interacts with the radiation field arises primarily by polarization of the collisional partner in the quadrupole field of one molecule: the free–free and bound–bound transitions originate from the same basic induction mechanism.

We will see below that, in general, van der Waals molecules have relatively few bound states. Under conditions commonly encountered (gas samples at not too low temperatures), many more free pair states than dimer states are populated. Therefore, the intensities of optical transitions involving a free initial state are generally much stronger than those involving bound initial states and these dominate the measurement.

Induced spectra actually consist of contributions arising from free-to-free, free-to-bound, bound-to-bound, and bound-to-free transitions. At temperatures much greater than the well depth of the intermolecular potential, $kT \gg \varepsilon$, the observed induced absorption is nearly fully due to free-to-free transitions as Welsh and associates suggest, but individual dimer lines or bands may still be quite prominent unless pressure broadening and perhaps other processes (like ternary interactions) have obliterated such structures. However, at lower temperatures, $kT \lesssim \varepsilon$, spectral components involving bound dimers become most prominent. In that case, the term 'collision-induced' is a poor choice.

In Welsh's first study [128], the shape of the absorption profile was found to be independent of the density of the gas if normalized by density squared, $\alpha(\nu)/n^2$, at nearly *all* frequencies ν. Pair spectra show no variation with density other than the density squared relationship – up to the point where ternary (or higher-order) spectra affect the measurements (if monomers are infrared inactive in the spectral band considered).

In an early paper, Condon [127] argued that in an external electric field all polarizable molecules will become infrared active, with selection rules known from Raman spectra ('field-induced absorption'). For homonuclear diatomics, this means that rotational transitions occur according to $J \rightarrow J+2$ (S-branch), $J \rightarrow J$ (Q-branch). and $J \rightarrow J-2$ (O-branch) if J represents the quantum number of the initial rotational state. Welsh *et al.* argue that collisional induction should have similar selection rules. The external field may be thought of as an intermolecular force field which is electric in nature. For molecules like O_2 and N_2, more or less ordinary Raman O, Q and S branches should be expected. Indeed, the measured spectra show the *envelopes* of these overlapping three Raman branches, Fig. 1.1. The rotational O lines are all to the left of the vibrational transition at 1556 cm^{-1}, and the S lines to the right; the vertical bars in the figure schematically represent the rotational lines observed in Raman studies. The Q branch, on the other hand, consists of a series of densely spaced lines near 1556 cm^{-1} that are often not resolved; only the envelope of the Q branch is indicated in the figure (dashed lines).

Apparently, within each branch, rotational lines are not resolved. This is due to the short interaction time of the collisional pair which renders individual lines rather diffuse, with half-widths that are much greater than the rotational spacings of O_2 and N_2 at temperatures around 300 K.

The spectral line shapes of collision-induced spectra (like in Fig. 1.3) resemble a Lorentzian, but the profile shown in Fig. 1.1 looks quite