Absolute Infrared Intensities for: Standards and Reactive Molecules

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1   Introduction

In recent years laser techniques have provided us with very accurate infrared line positions and the term "secondary frequency standard" has entered the lexicon of infrared spectroscopy. For example, line positions of carbon monoxide in the 5μm spectral region have been determined with an absolute accuracy of about 30 KHz [1]. Frequency information is prerequisite for obtaining accurate intensity information since the determination of transition dipole parameters from experimental intensity measurements requires numerical values for transition frequencies, transition initial state energies, and rovibrational partition functions. Transition frequencies are also used, along with quantum-mechanical models, to obtain the vibration-rotational state wave functions associated with the transitions of interest. The wave functions can then be used along with absolute or relative intensity information with an appropriate quantum mechanical model to determine parameters that describe the dipole surface of the molecule; some examples are for CO [2], OH [3] and CH_3Cl [4].

To the best of my knowledge, there are no reports of absolute line intensities of rovibrational transitions in the literature that could serve as secondary standards to an accuracy better than ±5%.

I estimate the absolute accuracy that currently could probably be obtained for secondary infrared intensity standards. Following that, I discuss intensity determinations for unstable molecular species. I do not attempt to give a rational for the level of accuracy needed for any particular application or propose specific molecules that could be candidates for use as secondary intensity standards.

2   Primary Intensity Standard

A "perfectly performing" spectrometer does not require a primary intensity standard in order to determine absolute line intensities from absorption measurements. Such an instrument responds linearly to photons over the appropriate radiative flux range and has negligible scattered light. However, were we to test the spectrometer's performance we would ultimately be limited by the accuracy of a primary radiation standard. I will assume here that a black body can serve this purpose. Blackbodies in operation at the National Physical Laboratory and the National Institute of Standards and Technology have emissivities equal to 0.999 or better and operate at temperatures known to about 200 millikelvin. At 5 μm our blackbody operating at 450K, with uncertainties in its temperature of 0.2 K and emissivity of 0.1%, would have an uncertainty in its emitted differential flux (Watts/cm^2-micron-sr) of 0.39%. The latter uncertainty depends on the

temperature of the blackbody and the precise wavelength, but for the purposes of the discussion to follow we will assume that our ultimate accuracy for infrared intensities is on the order of 0.4%.

In some cases it is possible to obtain absolute intensity information via relative intensity measurements over a large spectral interval, and in this situation a blackbody source is needed to establish the spectrometer's relative sensitivity with wavelength.

3   Secondary Intensity Standards

Secondary intensity standards have not been established for molecular infrared transitions, but in this section results obtained by our group are used to illustrate possible sources of errors in intensity determinations as well as expected accuracies which could be obtained from high-quality measurements.

The best way to determine the absolute intensity of rovibrational transitions of a stable molecule is with conventional absorption spectroscopy. The equations in the Appendix below show the relationships between the transmission of an individual rovibrational line (Eq. 1) and the rotationless transition moment for a rovibrational band (Eq. 3). The equations also indicate that accuracies of transition frequencies, energy levels, gas pressure, composition, broadening cross sections, absorbing path length, and temperature all play a role in determining the absolute accuracy of the measured transition moment, and therefore, the accuracy of any of these quantities will be a factor in determining the accuracy of the individual line intensities.

Table 1 shows the most precise results we have obtained to date for the rotationless transition moment of a rovibrational band. The four spectra of the $(00^02)_I$ $(00^00)_I$ band of $^{12}C^{16}O^{18}O$ were obtained using a natural abundance sample of carbon dioxide and the FTS at the National Solar Observatory, Kitt Peak, AZ. The double-sided interferograms produced excellent instrumental profiles in the spectral domain.

Table 1: Intensity data* for 4639.5 cm^{-1} band of $^{12}C^{16}O^{18}O$ determined via FTS spectroscopy (carbon dioxide in natural isotopic abundance).

Spectrum	Pressure (Torr)	Path (meters)	$\|<00^02\|M\|00^00>\|$ (Debye)
KP03	65.0	97.04	0.0014312
KP04	45.0	409.82	0.0014310
KP05	45.0	145.16	0.0014351
KP13	59.7	193.28	0.0014352

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The transition moments obtained from the individual spectra were obtained by plotting the square root of the reduced intensity of individual lines in the band vs. the m quantum number. The reduced line intensity is defined in Eq.(2) of the Appendix. The vibration-rotation interaction term is small enough to be undetermined; the precision of the transition moment squared determinations is ±0.15%. The individual line intensities used in the reduced intensity plots were obtained via non-

linear least-squares fitting of the FTS spectra. The paper of Benner *et al.* [5] gives a discussion of this technique which requires knowledge of the instrumental function as well as in this case the pressure broadening of $^{12}C^{16}O^{18}O$ by $^{12}C^{16}O_2$. The isotopic composition is obtained from a standard compilation [6], and the uncertainties for the above isotopes is negligible. At low pressures errors in pressure broadening are not as important as errors in the instrumental function and inherent errors in the pressure gauge or neglect of thermal transpiration [7] if the gas sample and capacitance manometer are at different temperatures. The pressure uncertainty of our measurements is about 0.22%. Our temperature uncertainty is about 0.17% which results in a 0.34% error (the rotational partition function is proportional to the temperature). This temperature error will also add an additional 0.17% error through the Boltzmann factor. Temperature errors can also cause an error in the vibration-rotation interaction term, F, of Eq.(7). If the compositional, path length, and data reduction errors can be assumed to be zero, the error in the absolute intensity would be about 0.75%. The latter estimate is clearly conservative in the sense that it is probably too low but is still greater than the precision of ±0.30% we have achieved for the above cited intensity measurements on $^{12}C^{16}O^{18}O$. It is probably reasonable to assume that we can achieve an absolute accuracy of about 2% in the determination of infrared rovibrational line intensities.

4   Unstable/Reactive Molecules

The determination of absolute intensities for reactive molecules is particularly difficult in the infrared because: (*i*) the sources that produce the spectra are usually not in LTE, except possibly for the lowest rotational levels, and (*ii*) the concentration of molecules in the optical path is not known. Lifetime techniques are not possible because the infrared radiative lifetimes are longer than collisional deactivation times.

For some diatomic molecules it has been possible to exploit the effect vibration-rotation interaction has on modifying intensities. Here knowledge of the abundance of the optically active species is not required, only the ratios of emission line intensities originating in common upper levels [3,8] or the relative intensities across an absorption band [9]. Eq.(3) taken in ratios is used for the emission experiments to determine the electric dipole moment function. The vibrational transition moment squared is determined from these measurements with absolute errors on the order of ±10%.

5   Conclusions

We have demonstrated that infrared line intensities can be determined with a precision of about 0.3%. For the particular experiment described the absolute error on the transition moment squared could be about 1%. It is probably reasonable to assume that we can achieve an absolute accuracy of about 2% in the determination of infrared rovibrational line intensities of stable molecules.

The absolute accuracies achieved for a small number of unstable molecules is on the order of ±10%.

6 Appendix

The equations which relate the absorption of radiation in an isolated rovibrational line (centered at the frequency ν_0) to its intensity is given by the Beer-Lambert Law,

$$\frac{I\left(\nu = \nu - \nu_0\right)}{I_0\left(\nu\right)} = \exp\left[-Spl\frac{H\left(\nu,Y\right)}{\nu_D}\left(\frac{\ln 2}{\pi}\right)^{1/2}\right], \tag{1}$$

where $I_0(\nu)$ and $I(\nu)$ are the intensities respectively, incident on and emergent from the absorbing gas sample. S is the line intensity, p the partial pressure of the species of interest, l the absorbing path length, and H the line shape. The Voigt line shape parameter, $Y = \left(\nu_L/\nu_D\right)\sqrt{\ln 2}$, is a function of the temperature and pressure. The Doppler broadening, ν_D, is a function of the molecular weight of the optically active species as well as the temperature. The pressure broadening coefficient, $\nu_L = \sum_i p_i \nu_{iL}^0 \left(T/T\right)^n i$, is a function of the temperature, $T(K)$, as well as the collisional cross sections between the various species, i. Here ν_{iL}^o is referenced to the standard temperature. The line intensity in Eq.(2) for

$$S_{if} = \frac{8\pi^3 N_L T_0}{3hc}\nu_0 \frac{G_{sr}}{Z_{vr}\left(T\right)T}\exp\left(\frac{-hcE_i}{kT}\right)\left[1 - e^{-hc\nu_0/kT}\right]\cdot HL\left(r_i,r_f\right)^{-1}$$

$$= S_{reduced} = \left|\left\langle v_i\left|M\left(Q_x\right)\right|v_f\right\rangle\right|^2 F\left(v_i,r_i;v_f,r_f\right) \tag{2}$$

a rovibrational transition between initial and final states, (i,f), depends on the temperature through the rovibrational partition function Z and exponential factors. T_0 is the standard temperature, N_L Loschmidt's Number and G_{sr} a statistical weight. The transition probability is factored into vibrational, rotational, HL, and rovibrational interaction terms, $\left|\left\langle v_i\left|M\left(Q_x\right)\right|v_f\right\rangle\right|^2 HL(r_i,r_f)F(v_i,r_i;v_f,r_f)$. Q_X represents an appropriate vibrational coordinate(s). The reduced intensity is related to the individual line intensities, S_{if} as well as quantities which can be calculated. A plot of $(S_{reduced})^{1/2}$ versus an appropriate rotational quantum number yields the vibrational transition moment as well as any dependence of the transition moment on rotational quantum numbers.

Unstable/reactive species molecular spectra are often observed in emission. The volume emission coefficient, I, is given by Eq.(3)

$$I = K\nu^4 N_i e^{-\left(E_i/kT\right)}\left|\left\langle i\left|M\right|f\right\rangle\right|^2 \tag{3}$$

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